REMOVAL OF WATER VAPOUR FROM NATURAL GAS
BY USING MEMBRANE SEPARATION (STUDY ON
PERCENT OF WATER VAPOUR REMOVAL)

SITI NOOR LAILA BINTI MAT RASID

CHEMICAL ENGINEERING
UNIVERSITI TEKNOLOGI PETRONAS
JULY 2008

Removal of Water Vapour from Natural Gas by Using Membrane Separation (Study on Percent of Water Vapour Removal)

by

Siti Noor Laila Binti Mat Rasid

Dissertation report submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

JULY 2009

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Removal of Water Vapour from Natural Gas by Using Membrane Separation

(Study on Percent of Water Vapour Removal)

by

Siti Noor Laila bt Mat Rasid

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

(Dr. Lau Kok Keong)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

July 2009

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

SITI NOOR LAILA BT MAT RASID

ABSTRACT

The purpose of this report is to study on 'The Removal of Water Vapour from Natural Gas by Using Membrane Separation'. This report includes the objectives, scopes of study, problem statement, literature review, methodology, results, discussion, conclusion and recommendations.

The main objective of this project is to analyze the performance and efficiency of membrane to remove water vapour from natural gas. Literature review is studied to obtain the properties and characteristics of flat membrane. Experimental lab is conducted to test the performance of the membrane under various operating pressure.

Membrane is selected since it requires smaller space, thus it will be easier to be installed at offshore platforms. Organic and inorganic membranes are widely used in gas separation industry, especially to remove nitrogen and carbon dioxide from natural gas. A lot of research done show that membrane has big potential in removing water vapour from natural gas. Thus, in this project, apart from studying the properties of membrane, characterizations and dynamic performance of the selected membrane is also studied by conducting experimental lab. The membrane used in this project is Polaris^{TM} membrane, supplied by MTR Inc.

Three experiments have been conducted to determine the characteristics of the membrane. Scanning Electron Microscopy (SEM) is used to observe the morphology of the membrane. From the image obtained, it is concluded that the membrane is asymmetry and classified as an integrally skinned and dense top layer membrane. Fourier Transform Infrared (FTIR) spectroscopy is used to get the information of all the components in the membrane. The data gives the plot of transmitter versus wavelengths. Based on the wavelengths, we analyse the components of the membrane. From the results, we found that the membrane has more than three functional groups. The analysis of the FTIR result is still in progress. The last characterization conducted was Thermo Gravimetric Analysis (TGA), which was to determine the degradation temperature of the membrane. The result shows that the membrane can stand and can be operated at high temperature until the maximum temperature of 430.60°C.

For parametric analysis, calibration has been conducted to determine the best operating temperature for the experiment. Temperature is constant in the experiment, thus calibration is needed to choose the best temperature. From calibration curve, temperature of 50°C is selected.

For performance experiment conducted with Gas Separation Unit, the pressure is varied from 10 bar to 40 bar, with constant temperature of 50°C and flow rate of 5 LPM. The performance of membrane is analyzed by evaluating the percentage of water vapour removal and hydrocarbon loss. The target is to get high water vapour removal and low hydrocarbon loss.

The percentage of water vapour removal from methane and hydrocarbon loss under various pressures is plot. It is observed that the removal of water vapour increases as pressure increases, which means the membrane separate more water vapour from methane at high pressure. Unfortunately, the percentage of hydrocarbon loss also increases as the pressure increases. Thus, it is recommended for next study that optimization is to be conducted based on cost analysis in order to minimize hydrocarbon loss and maximize water vapour removal by the membrane.

As the conclusion, the objective of this project to analyze the performance of the membrane is achieved. The flat membrane used in this project is classified as asymmetry, integrally skinned and dense top layer membrane. The membrane consists of mainly O-H, N-H, C=O and C- H functional groups. The degradation temperature of the membrane is 430.60°C. As for performance analysis, it is obtained that the percent of water vapour removal and hydrocarbon loss increase as the pressure increases.

ACKNOWLEDGEMENTS

The author would like to express her gratitude to almighty God for allowing author to complete this Final Year Project (FYP), and keeping author healthful all the time. And also would like to take this exceptional opportunity to honourably thank the FYP Committee, Chemical Engineering Department, Universiti Teknologi PETRONAS (UTP) for giving author this chance to learn and experience a research work and for all their support and integrity which played an ultimate roll in the success of this project.

Upon completing one year of this Final Year Project, author is indebted to main supervisor, Dr. Lau Kok Keong and also Post Graduate student, Ms Najmin who give great innovation and ideas to complete this final year project. Special thanks dedicated to both of them to help and support author so much during this difficult time.

Author also would like to give appreciation mostly to all the lab technicians from Chemical and Mechanical Department for helping in doing lab work. It would be impossible to complete this Final Year Project without the help from all of them.

Author hope all the experiences and skills gained during this project will be useful for the future and real working environment soon. Last but not least, thank you very much.

TABLE OF CONTENTS

ABSTRACT i

ACKNOWLEDGEMENTS iii

CHAPTER 1: INTRODUCTION

1.1 Project Work Background 1
1.2 Problem Statement 3
1.3 Objectives of Study 4
1.4 Scope of Study 4

CHAPTER 2: LITERATURE REVIEW

2.1 Membrane Technology 6
2.2 Classification of Membranes 6
2.3 Types and Modules of Membrane 9
2.4 Characterizations of Membrane 11
2.5 Solution – Diffusion Model 13
2.6 Percent of Water Vapour Removal 16
2.7 Percent of Hydrocarbon Loss 17
2.8 Cost Analysis Of Membrane System 17
2.9 Nitrogen Removal From Natural Gas Using Membranes 20

CHAPTER 3: METHODOLOGY

3.1 Literature Review 24
3.2 Characterization 24
3.3 Parametric Analysis 27

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Characterizations Study 29
4.2 Parametric Analysis 34

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion 39
5.2 Recommendations 40

REFERENCES 41

APPENDICES 43

LIST OF FIGURES

Figure 1: Natural Gas Processing.....2
Figure 2: One example of TEG system.....3
Figure 3: Classification of typical membrane morphology.....7
Figure 4: Schematic representation of symmetric membrane cross-section 7
Figure 5: Schematic representation of asymmetric membrane cross-section.....8
Figure 6: The relative size and condensability (boiling point) of the principle components of natural gas.....10
Figure 7: Mullen Burst Testing Machine.....11
Figure 8: Scanning Electron Microscopy (SEM) machine.....12
Figure 9: Bubble point test.....13
Figure 10: Schematic diagram of gas separation by membrane.....14
Figure 11: Schematic diagram of membrane module.....16
Figure 12: Direct CAPEX comparison between membrane and TEG system.....18
Figure 13: Allocated platform cost of membrane and TEG system.....18
Figure 14: Manpower, routine maintenance and chemical agents cost for membrane and TEG system.....19
Figure 15: Energy cost comparison between membrane and TEG system.....20
Figure 16: Methane/nitrogen selectivity as a function of feed temperature for the PTMSP membrane 22
Figure 17: Scanning Electron Microscopy (SEM) 25
Figure 18: Fourier Transform Infrared (FTIR) spectroscopy 26
Figure 19: Thermogravimetric Analysis equipment 26
Figure 20: Gas Separation Unit.....28
Figure 21: Top surface image of membrane observed by using SEM with magnification of 10 K X 29
Figure 22: Top surface image of membrane observed by using SEM with magnification of 50 K X 29
Figure 23: Cross section structure of membrane observed by using SEM with magnification of 100 X 30

Figure 24: Cross section structure of membrane observed by using SEM with magnification of 500 X 30
Figure 25: Plot of transmitter (%) versus wavelength obtained from FTIR 31
Figure 26: Plot of weight percent (%) versus temperature (°C) obtained from TGA.....33
Figure 27: Plot of moisture content versus pressure at different inlet temperature.....35
Figure 28: Plot of water removal percentage at different inlet pressure.....36
Figure 29: Plot of hydrocarbon loss at different inlet pressure.....37
Figure 30: Comparison between water removal and hydrocarbon loss.....38
Figure 31: Plot of weight (mg) versus temperature (°C) obtained from TGA.....52

LIST OF TABLES

Table 1: Various uses of natural gas in various sectors.....1

Table 2: Materials for gas separation membranes.....9

Table 3: The disadvantage of olefinic polymer, poly(siloctylene-siloxane) and Teflon AF.....21

Table 4: Membrane Materials Chosen for Feasibility Study for Denitrogenation of Natural Gas.....21

Table 5: Summary of permeability and selectivity of the three membranes tested 22

Table 6: Components and functional group analyzed from FTIR data.....32

Table 7: Inlet moisture content at various temperature and pressure.....34

Table 8: Percentage of water vapour removal at various inlet pressures.....36

Table 9: Percentage of hydrocarbon loss at various inlet pressures.....37

Table 10: Functional groups with their wavelengths used for FTIR data analysis.....43

Table 11: Data table of temperature and weight percent of membrane obtained from TGA 50

Table 12: Data table of temperature and weight of membrane (mg) obtained from TGA 51

CHAPTER 1
INTRODUCTION

1.1 PROJECT WORK BACKGROUND

The demand of natural gas in industry is increasing rapidly. Natural gas is used by a variety of sectors such as industrial sector, residential, commercial use, transportation sector and power generation. In industrial sector, it provides the base ingredient for plastics, anti-freeze and fabrics. It is consumed primarily in the pulp and paper, metals, chemicals, petroleum refining, stone, clay and glass, plastic, and food processing industries. Natural gas is used in power generation as a major source of electricity generation. The main uses of natural gas in residential and commercial sector include space heating, water heating, and cooling. For restaurants and other establishments that require cooking facilities, natural gas is a popular choice to fulfil these needs. In transportation sector, natural gas is used as the alternative fuel for the vehicle. Natural gas vehicles as they exist today are best suited for large fleets of vehicles that drive many miles a day. Taxicabs, transit and school buses, airport shuttles, construction vehicles, garbage trucks, delivery vehicles, and public works vehicles are all well suited to natural gas fuelling (Wikipedia, 2009).

Table 1: Various uses of natural gas in various sectors

Sector	Uses
Industrial	• Provides the base ingredient for plastics, anti-freeze and fabrics. • Consumed primarily in the pulp and paper, metals, chemicals, petroleum refining, stone, clay and glass, plastic, and food processing industries
Power generation	A major source of electricity generation
Residential and commercial	Space heating, water heating, and cooling
Restaurants	Cooking facilities
Transportation	Alternative fuel for the vehicle

Natural gas consists of primarily methane component. Other than methane, raw natural gas that comes out from the wells is actually consists of by-products such as propane, ethane, butane, pentanes, water vapour, hydrogen sulphide (H_2S), carbon dioxide, helium, nitrogen, and other compounds. Before it can be used it industry, it has been purified to remove all the contaminants in it. It must undergo a few processes before it is sold to industry. The flow diagram of natural gas processing is shown below:

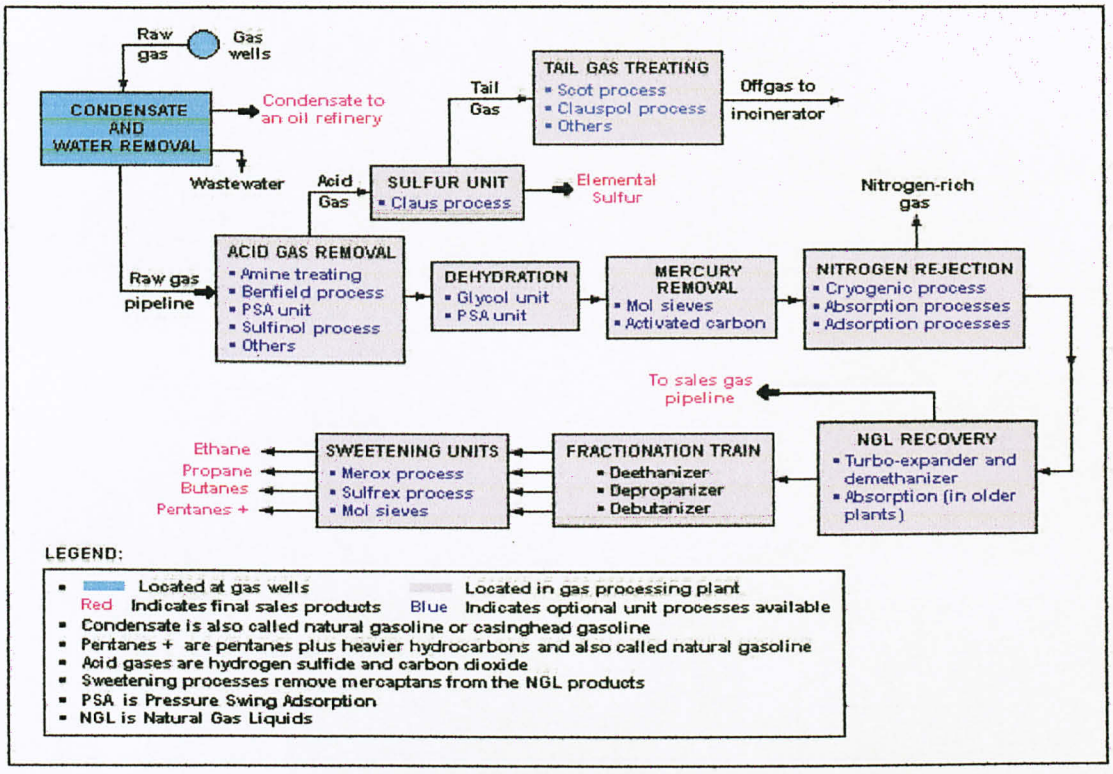


Figure 1: Natural Gas Processing

One of the processes in natural gas processing is to remove water vapour from natural gas. Water should be removed from natural gas since it can cause operational problems. Water component can associate with carbon dioxide or hydrogen sulphide to form carbonic acid and cause corrosion to the pipeline.

The most common system has been used in this process is absorption process by using tri-ethylene glycol (TEG) system. Glycol solution is brought into contact with wet gas stream in a contactor. The glycol solution will absorb the water vapour from the wet gas. Once absorbed, the glycol particles become heavier and sink to the bottom of the contactor where they are removed. The natural gas, having been stripped of most of its water content, is then

transported out of the dehydrator. The glycol solution, bearing all of the water stripped from the natural gas, is put through a specialized boiler designed to vaporize the water out of the solution. While the water reaches a boiling point of 212 degrees Fahrenheit, glycol does not boil until 400 degrees Fahrenheit. The difference of their boiling point makes it relatively easy to remove water from the glycol solution, allowing it to be reused in the dehydration process.

1.2 PROBLEM STATEMENT

The most commonly system used in industry to remove water vapour from natural gas is trietylene glycol (TEG) system. This is an absorption process where water from natural gas is absorbed by glycol solution and removed by using boiling point difference principle.

Figure 2: One example of TEG system

There are a few problems faced by TEG system. Suspended foreign matter, such as dirt, scale and iron oxide may contaminate glycol solutions. There are also substantial environmental problems due to fugitive emissions, soil contamination and fluid disposal problems.

Another major problem is regarding the space needed to install the system. TEG is the current system used at offshore platforms to remove water vapour from natural gas. The problem is TEG needs a big space for installation at offshore platform. Offshore platform has

very limited space and even the equipments are located very close to each other. Thus we aim to find another system which is more compact and can remove water vapour effectively.

To overcome this problem, research need to be done to find other alternatives that will work as effective as TEG system. One of the alternatives is by using gas separation membrane.

Membranes have been used widely to remove acid gases from natural gas, e.g. the separation of carbon dioxide from natural gas by using polycarbonate membrane. There is a big potential for the membrane to remove water vapour from natural gas effectively. To know the types of membrane that is suitable for this process, properties of each type of membrane will be studied and experiment will be conducted to test the performance and determine the best operating conditions of the selected membrane. Thus we need to test the performance of membrane in removing water from natural gas.

1.3 OBJECTIVES OF STUDY

The main objectives of this study are:

1) To study the characterizations of membrane to determine its properties and behaviours.
2) To study the performance of membrane by evaluating the removal of water vapour.
3) To analyze the effect of pressure on the percentage of water removal and hydrocarbon loss.

1.4 SCOPE OF THE STUDY

This project will focus on the membrane properties since it will determine the behaviours of the membrane. Research will be done to determine the type and module of membrane to be used. All the limitations of membrane will be obtained from literature study in order to determine the minimum and maximum operating conditions of the membrane. Dynamic performance of membrane will be analyzed from experimental results to determine the operating parameters of the process.

Once the type and module of membrane is determined and the membrane is available, experimental lab will be conducted to test the performance of the selected membrane. The efficiency of the membrane to remove water from natural gas will be tested under various operating pressure. According to the results obtained, the performance of the membrane is analyzed.

CHAPTER 2
LITERATURE REVIEW

2.1 MEMBRANE TECHNOLOGY

Membrane gas separation has emerged in the chemical industry in the last 30 years (S.P. Nunes and K.-V. Peinemann, 2001). Membrane is a semi permeable material that allows only certain molecules to pass through it (Cristie John Geankopolis, 2003). It is widely used in industry for producing oxygen-enriched air for individual medical applications, removal of carbon dioxide from natural gas, ethanol purification and so on.

In separation process, phase change increases significant energy cost to the cost of separation. By using membrane, no phase change is required. In addition, membrane system is small in size compare to other equipments like TEG and amine unit, thus require smaller footprints. The criterion is important in environment such as offshore gas-processing platform. Another advantage of membrane is the lack of mechanical complexity in membrane systems (Chemical and Engineering News, 3rd October 2005, *Membranes for Gas Separation*).

2.2 CLASSIFICATION OF MEMBRANE

Membrane morphology can be classified into two classes; symmetric and asymmetric (Mulder, 1996). Symmetric membrane is the membrane that has uniform structure and transport properties throughout its thickness. A membrane which has two or more structural planes of non-identical morphologies is called asymmetric membrane (Koros, et al, 1996). Figure 3 shows the classification of typical membrane morphology.

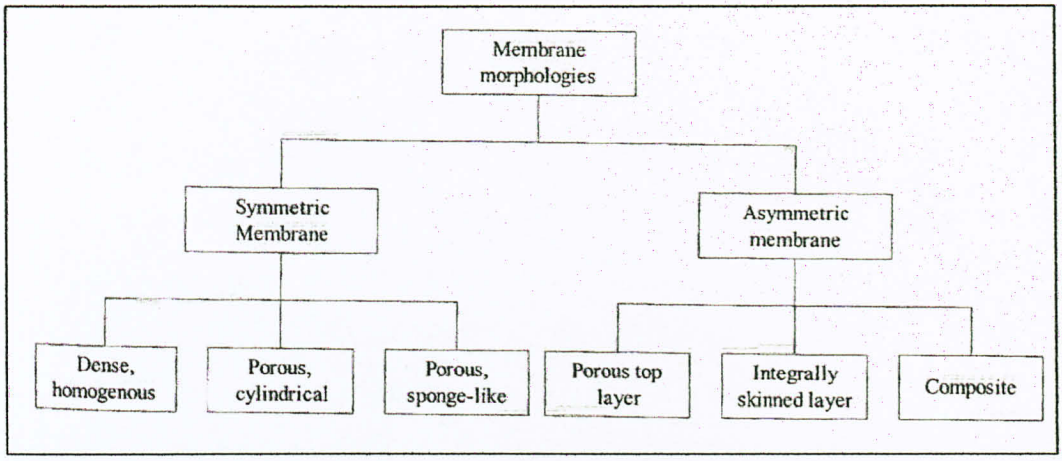


Figure 3: Classification of typical membrane morphology.

Symmetric membrane is classified into three types:

1. **Cylindrical porous membrane** - This type of membrane constitutes of finger-like structure that is usually used in small size laboratory experiments, etc. DNA separations from dilute solutions and enzyme.
2. **Homogeneous dense membrane** – This membrane has a dense film structure through in which permeates are transported by diffusion under the driving force of a pressure, concentration or electrical potential gradient (Baker, 2004). It is used in gas separation study and applied in pervaporation (Chen, 2002).
3. **Sponge-like porous membrane** – This membrane is often used for micro filtration. It consists of sponge-like closed structure and has the average pore size of 0.2-5 μm (Chen, 2002).

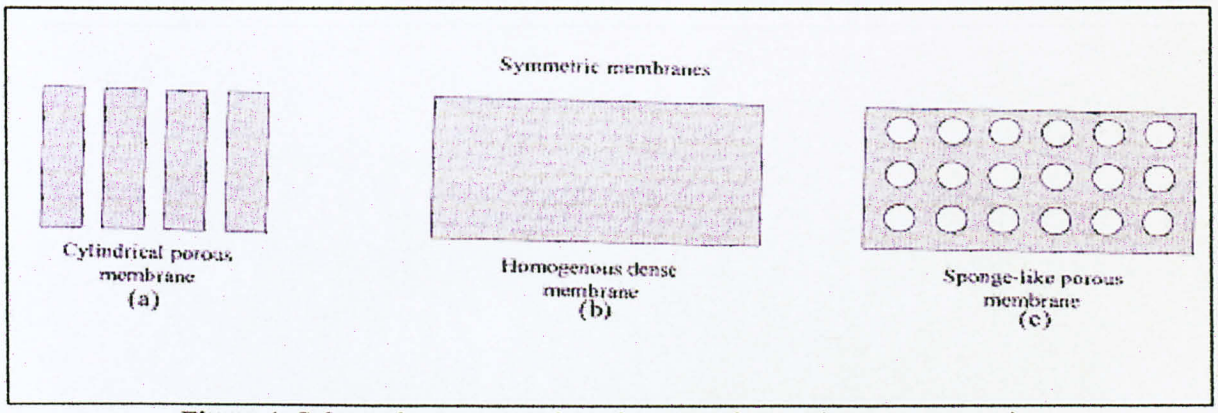


Figure 4: Schematic representation of symmetric membrane cross-section

For asymmetric membrane, it can be divided into three groups:

1. **Porous top layer membrane** – The pore size of the membrane is increasing from top to bottom. This membrane is usually used in ultrafitlration and microfiltration field (Chen, 2002).
2. **Integrally skinned and dense top layer membranes** – This type of membrane is often used in gas separation (Chen, 2002). It constitutes of dense thin layer (thickness 0.1-0.5 μm) supported with the porous substructure (thickness 50-150 μm).
3. **Composite membrane** – This membrane consists of dense layer which is placed on top of a support membrane, where both dense layer and support membrane are made from different materials. This type of membrane is normally used in gas separation and pervaporation (Chen, 2002).

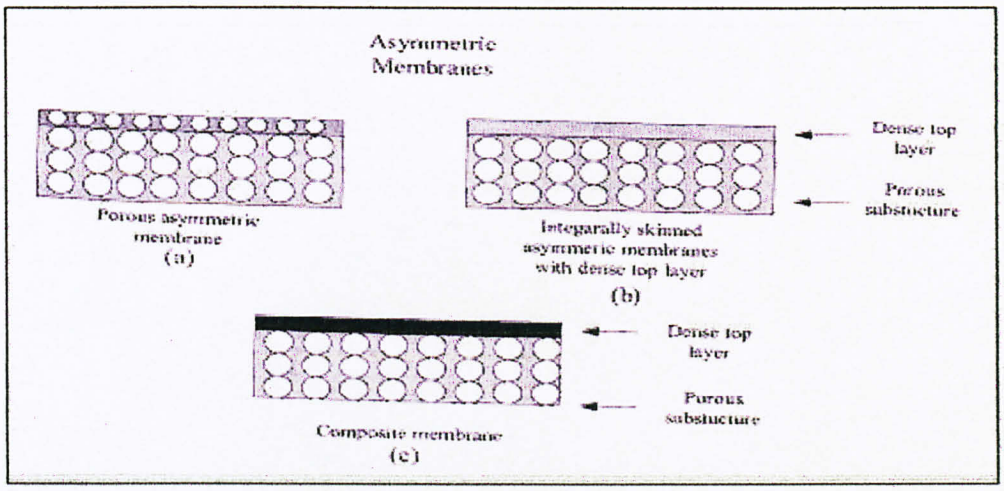


Figure 5: Schematic representation of asymmetric membrane cross-section

The study of membrane morphology is useful in determining the performance and application of membrane. For membrane, high total flux and selectivity is desired. Symmetric membrane has high selectivity, but low in total flux. Thus it is commonly prepared and researched in laboratory scale. Asymmetric membrane has been used commercially in various industries since it has high total flux with sufficient selectivity.

2.3 TYPES AND MODULES OF MEMBRANE

There are various types of membrane available for gas separation. Most of the gas separation membranes made of polymers and formed as flat sheets or hollow fibres. Many polymers have a high permeability of water vapour and several materials have been used to make membrane intended for certain dehydration uses. In this project, flat typed membrane will be used. It is easy to fabricate and use flat membrane and the area of the membrane is well defined. The structure of flat module membrane is simple and the replacement is easy (Takeshi Matsuura, 1993).

Polymers can be easily processed into membranes. Organic polymer membranes are commonly used in gas separation process, since they have sufficient gas selectivity. For inorganic membranes, even though the market demand are small, there are a few advantages of using inorganic membrane; the possibilities of cleaning with steam, high pressure up to 10 MPa can be applied and has a good back flushing to remove fouling.

Table 2: Materials for gas separation membranes.

Organic Polymers	**Inorganic Materials**
Polysulfone, polyethersulfone	Carbon molecular sieve
Celluloseacetate	Nanoporous carbon
Polyimide, polyetherimide	Zeolites
Polycarbonate (brominated)	Ultramicroporous amorphous silicia
Polyphenyleneoxide	Palladium alloys
Polymethylpentene	Mixed conducting perovskites
Polydemethylsiloxane	
Polyvinyltrimethylsilane	

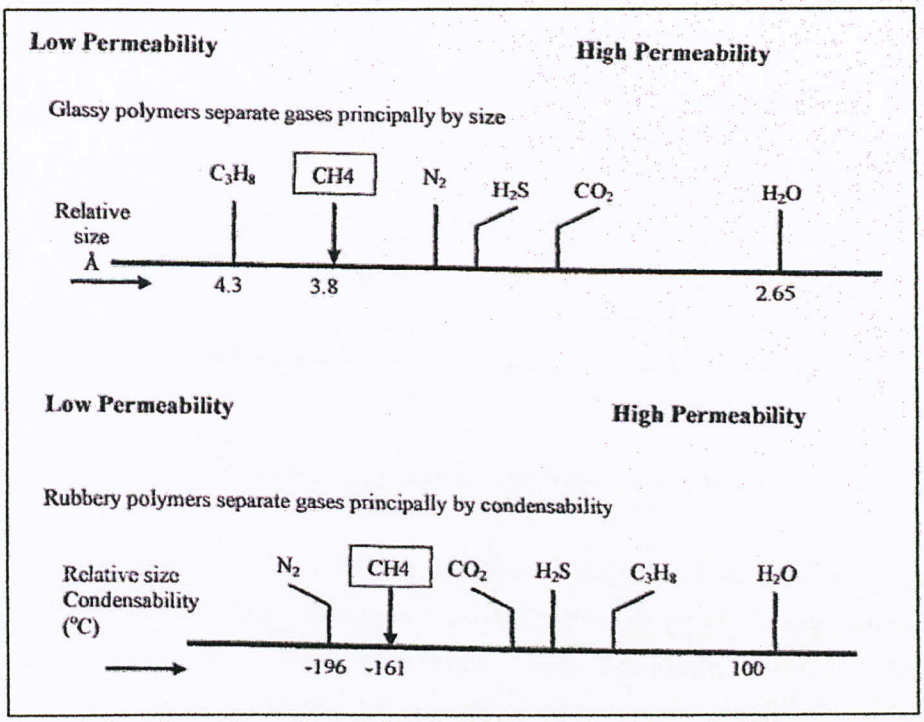


Figure 6: The relative size and condensability (boiling point) of the principle components of natural gas.

From figure 6, water has the smallest size in natural gas and the most condensable. Thus water is easily separated from natural gas by both glassy and rubbery polymers (Nur Zuraini, 2003). Glassy polymeric membrane separates gas principally by size. In natural gas composition, water vapour has the smallest molecular size (relatively 2.65 Å). Thus water vapour will be the permeate (component that passes through the membrane) and other components in natural gas will be the retentate (component that can not pass through the membrane).

Glassy polymeric membrane is one of the best membranes for gas separation. It is very useful to separate one of the components from gas mixture such as hydrogen, helium, oxygen, nitrogen, carbon dioxide, carbon monoxide and water vapour. It is effective in gas separation when one of the gas components has high solubility in the glassy polymer and high diffusivity through the glassy polymer (Yoshihito Osada and Tsutomu Nakagawa, 1992).

Glassy polymeric membrane are made of various types of polymers such as polysulfone, polyimides etc. By far, cellulose acetate, polysulfone and polyimides are the most important polymers for gas separation membranes. Among them, polysulfone membrane

is the most effective in removing water from natural gas since it has high permeability and selectivity.

Gas separation membranes usually operate under continuous steady-state conditions with three streams. The feed stream is a high-pressure gas mixture that passes along one side of the membrane. The molecules that pass through the membrane is called permeate stream. The non-permeating molecules that remain on the feed-stream side exit the membrane as the retentate stream. The permeation process is driven by pressure difference across the membrane.

For a dense polymer film, the flux through the membrane is inversely proportional to the thickness. Thus, there is a strong incentive to make the membrane as thin as possible without having holes or weak spots in it. Since gas separation processes operate based on pressure difference, the natural gas in the feed stream is compressed to provide the driving force for the separation.

2.4 CHARACTERIZATIONS OF MEMBRANE

There are a few techniques used to measure properties of membrane. Some of the properties are porosity, pore size, pore distribution, strength and permeability.

2.4.1 Strength Test

The Mullen burst test is used to test the strength of a membrane. The membrane is placed over a rubber bladder. The bladder is then filled with oil cause the membrane to stretch. The pressure when the membrane ruptures is recorded (Keith).

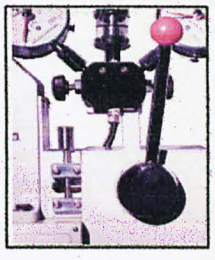


Figure 7: Mullen Burst Testing Machine

2.4.2 Porosity

Pore statistics of a membrane can be observed by using Scanning Electron Microscopy (SEM) image. The image will show overall view of the membrane structure, top and bottom surfaces and cross section. This enables any symmetry to be observed. SEM method is used to study the surface of micro filtration membranes since the resolution limit lies in the region of 0.01 μm (Keith).

Figure 8: Scanning Electron Microscopy (SEM) machine

2.4.3 Permeability

To determine the pore size of a membrane, the relationship between pressure difference and flux of fluid through the membrane need to be measured. For a real membrane, a non-uniform distribution of pore exists. After the breakthrough pressure is reached for the large pores, more of smaller pores become permeable. It will result in a non-uniform variation of flux with pressure, up to a maximum pressure where all the pores are active. The characteristic of the membrane pore distribution is represented by the flux-pressure drop (Keith).

2.4.4 Pore Size

Bubble point test is used to determine the pore size of a membrane. The membrane is wet with alcohol and the surface of the membrane is allowed to be visible under a thin layer of wetting solvent. The pressure of the gas is increased slowly. The bubble point is the pressure where gas can be seen bubbling through the membrane. The bubble point is related to the pore size of membrane by Young and Laplace equations (Keith).

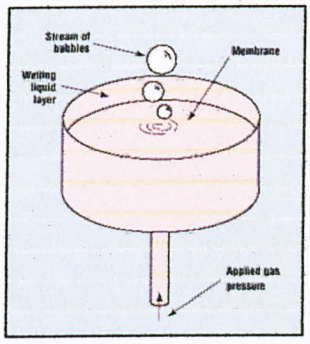


Figure 9: Bubble point test

2.5 SOLUTION – DIFFUSION MODEL

Solution-diffusion model is the simplest model used to explain and predict gas permeation through non-porous polymers. It is assumed that the gas at the high pressure side of the membrane dissolves in the polymer and diffuses down a concentration gradient to the low pressure side, where the gas is desorbed. It is also assumed that sorption and desorption at the interfaces is fast compared to the diffusion rate in the polymer. The gas phase on the high and low pressure side is in equilibrium with the polymer interface (S.P. Nunes and K.-V. Peinemann, 2001).

The combination of Henry's law (solubility) and Fick's law (diffusion) forms this equation:

$$J = \frac{D * S * \Delta p}{l}$$

and

$$P = D * S$$

This can be simplified to

$$J = \frac{P * \Delta p}{l}$$

Where D is the diffusion coefficient of the gas in the polymer, S is the gas solubility, Δp is the pressure difference between high and low pressure side, l is the membrane thickness and P is the permeability coefficient (S.P. Nunes and K.-V. Peinemann, 2001).

One parameter which determine the gas enrichment is the membrane selectivity α, which is a membrane property and defined as $\alpha = P_2/P_1$ with P_2 and P_1 as permeability

coefficient for gas 1 and gas 2. Other important parameters are the stage cut θ and the pressure ratio Φ. The stage cut is defined as ratio of permeate flow/feed flow and the pressure ratio is the ratio of total feed pressure to total permeate pressure. To simplify the equation, a stage cut is set to be close to zero, i.e. there is no concentration difference between feed and retentate. The maximum enrichment of the faster component 2 can now be determined easily. For the maximum enrichment the maximum driving force is needed, i.e. the permeate pressure can be neglected when compared to the feed pressure. The flux of component 1 is proportional to its volume fraction on the feed side, for component 2 we have, as an additional factor the membrane selectivity (S.P. Nunes and K.-V. Peinemann, 2001).

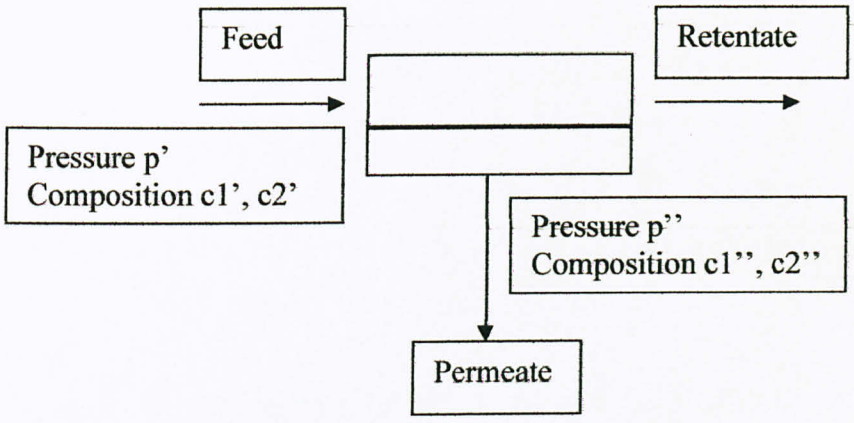


Figure 10: Schematic diagram of gas separation by membrane

$$J1 = const. \times c1' = const. \times (1 - c2')$$

$$J2 = const. \times \alpha \times c2'$$

The concentration of component 2 on the permeate side must be equal to the flux J_2 of component 2 divided by the total flux J_1+J_2. Combining the two equations yields

$$c2'' = \frac{c2' \times \alpha}{1 + c2'(\alpha - 1)}$$

This simple equation gives the maximum possible enrichment of one gas of a two component mixture when separated by a membrane with a selectivity of α. The equation becomes more complex when the permeate pressure cannot be neglected. Following the simple solution-dilution model of the gas fluxes for gas 1 and gas 2 through the membrane are

$$J1 = \frac{P1(p1' - p1'')}{l}$$

and

$$J2 = \frac{P2(p2' - p2'')}{l}$$

Where P1 and P2 are the permeabilities of components 1 and 2, l is the membrane thickness, and p1', p1" and p2',p2" are the partial pressure of the two gases in the feed and permeate streams, respectively. The total gas pressure is equal to the sum of the partial pressure, i.e.

$$p' = p1' + p2'$$

$$p'' = p1'' + p2''$$

with

$$c2' = p2'/p' \qquad c2'' = p2''/p''$$

and

$$J1/J2 = c1''(1 - c1'') = (1 - c2'')/c2''$$

Combining all equations yields

$$c2'' = 0.5\phi[c2' + \frac{1}{\phi} + \frac{1}{\alpha - 1} - \sqrt{(c2' + \frac{1}{\phi} + \frac{1}{\alpha - 1}) - \frac{4c2'\alpha}{\phi(\alpha - 1)}}$$

This equation gives the concentration of the faster permeating gas in the permeate stream as the function of the membrane selectivity and the pressure ratio across the membrane. It breaks down into two limiting cases. At high driving forces when the pressure ratio is much higher than selectivity ($\Phi >> \alpha$) the equation reduces to

$$c2'' = \frac{c2' \times \alpha}{1 + c2'(\alpha - 1)}$$

It is called a selectivity controlled region, because the enrichment is now independent of the pressure ratio. When on the other hand, the pressure ratio becomes much smaller than the selectivity ($\Phi << \alpha$), the equation reduces to

$$c2'' = c2'\phi$$

The enrichment now is independent of the membrane selectivity. Hence, this is the pressure ratio limited region. There is, of course, an intermediate region between these two limiting cases where both the pressure ratio and the membrane selectivity affect the degree of separation (S.P. Nunes and K.-V. Peinemann, 2001).

2.6 PERCENT OF WATER VAPOUR REMOVAL

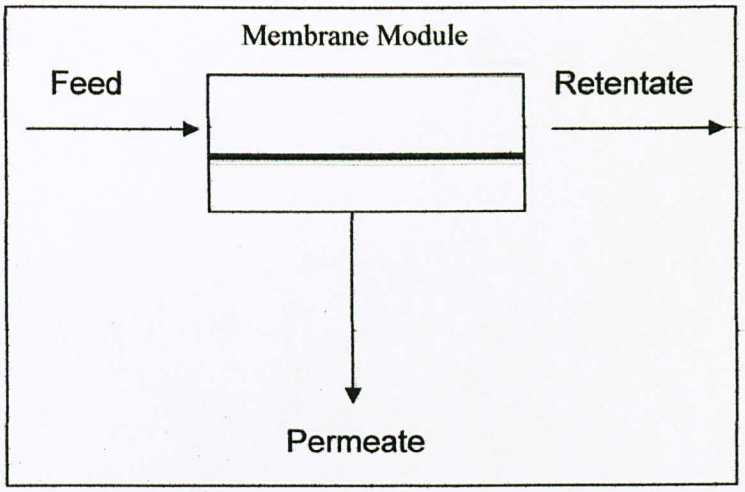


Figure 11: Schematic diagram of membrane module.

The retentate is the desired product, which is the methane. The permeate will be the water vapour since water vapour can pass through membrane. The formula to calculate the percent of water vapour removal by membrane is given by:

$$\frac{\text{Water concentration in the membrane inlet} - \text{water concentration in the retentate outlet}}{\text{Water concentration in the membrane inlet}} \times 100\%$$

2.7 PERCENT OF HYDROCARBON LOSS

Hydrocarbon loss is defined as the amount of hydrocarbon that passes through membrane along with water vapour. Since the hydrocarbon is the desired product, we want the hydrocarbon loss to be as low as possible. The formula to calculate the percent of hydrocarbon loss is given by:

$$\frac{\text{Flow rate of membrane inlet} - \text{Flowrate of permeate}}{\text{Flow rate of membrane inlet}} \times 100\%$$

2.8 COST ANALYSIS OF MEMBRANE SYSTEM

A study has been done by F.Binci, F.E. Ciarapica and G.Giacchetta to compare between traditional glycol plants and innovative membrane system for dehydration of natural gas in offshore rigs. From the research, a comparison of cost between glycol and membrane system is made. The allocated platform cost, CAPEX and OPEX of membrane system is compared with three types of gylcol system, which are high pressure column TEG, low-pressure column and low temperature TEG, and low-pressure column and high temperature TEG. From the comparisons made, it is obtained that membrane system does have lower cost than TEG system under certain conditions.

In comparing the CAPEX, the expenses incurred for the construction and installation of all the systems have been analyzed. The direct cost items (costs of separation equipment, ancillary equipment and installation) and the indirect cost items (engineering and allocated platform cost) was studied.

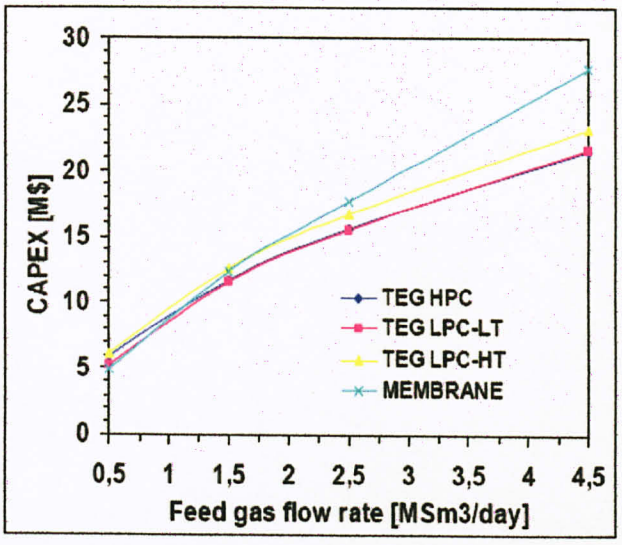


Figure 12: Direct CAPEX comparison between membrane and TEG system

From the results obtained for CAPEX comparison, it is concluded that membrane system has lower CAPEX when the feed gas flow rate is low. As the feed gas flow rate increases, the CAPEX of membrane system also increases. For higher feed gas flow rate, membrane system has the highest CAPEX compared to TEG system (F.Binci, F.E. Ciarapica and G.Giacchetta).

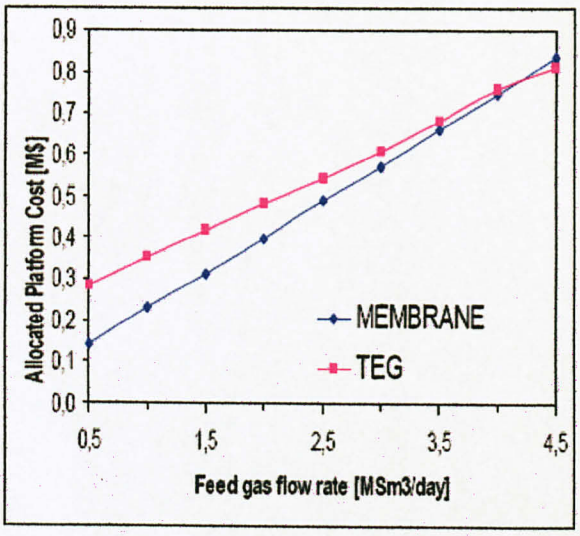


Figure 13: Allocated platform cost of membrane and TEG system

The allocated platform cost of membrane and TEG system represent the cost of the part of platform occupied by the dehydration plants, because the sizes and weights of the

systems being compared were very different and their reduction should always be pursued. It can be observed that allocated platform cost of membrane system is lower than TEG system for low feed gas flow rate. At higher gas feed flow rate, the platform cost of membrane system is higher that TEG system. This shows that that membrane plants enable a considerable saving in terms of the weight and size of the installation for low feed gas rates. As the plant's size grows, the number of membrane module that have to be installed increases as well, thus increase the size and weight of membrane skid compared to TEG plant. In term of allocated platform cost, membrane system is economically viable for small platforms, where the gas feed flow rate is low and the space available for gas dehydration is limited. For higher gas feed flow rate, TEG system is more econmicaly viable than membrane system (F.Binci, F.E. Ciarapica and G.Giacchetta).

For OPEX comparison, the expenditure involved in operating the platform throughout its lifetime is analyzed. The cost items include manpower cost, chemical agent, routine maintenane, extraordinary maintenance and energy cost.

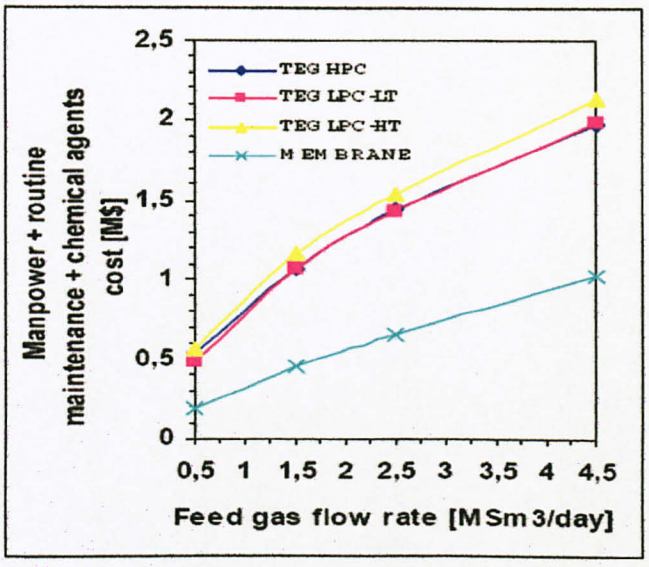


Figure 14: Manpower, routine maintenance and chemical agents cost for membrane and TEG system.

From the result, it is concluded that for all range of feed gas flow rate, membrane system has lower manpower, routine maintenance and chemical agents cost compared to TEG system. Membrane system if found to enable evident saving regardless of the range of feed gas flow rate (F.Binci, F.E. Ciarapica and G.Giacchetta).

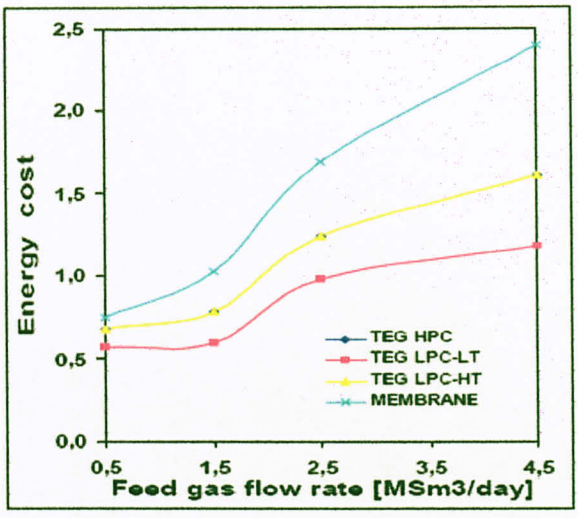


Figure 15: Energy cost comparison between membrane and TEG system

Based on energy cost analysis, it is concluded that energy cost of membrane system is more expensive than TEG system. Membrane system use compressors and the cost of energy to work for compressor systems are high.

The economic assessment showed that membrane dehydration system at offshore platforms could be better value for money than the TEG depending on predicted membrane lifetimes, feed gas flow rates and the operating conditions of the platform (F.Binci, F.E. Ciarapica and G.Giacchetta).

2.9 NITROGEN REMOVAL FROM NATURAL GAS USING MEMBRANES

A research on denitrogenation of natural gas by using membrane has been done by Membrane Technology and Research Inc. The study used high-performance methane-permeable membrane at low temperatures to separate the feed gas stream into a methane-rich product stream, and a nitrogen-rich waste gas stream. From literature, a methane/nitrogen selectivity of 4-6 would be sufficient for a methane-permeable membrane to be viable (Kaaeid A. Lokhandwala, Matt Ringer, Hans Wijmans and Richard W. Baker). The objective of the project is to determine whether the target selectivity can be achieved and determine whether the membrane will be technically and economically viable.

Six polymers were selected as candidate materials for denitrogenation membrane which includes polyamide-polyether copolymer, an olefinic polymer, silicone rubber, poly(siloctylene-siloxane), poly(trimethylsilyl propyne)[PTMSP], and Teflon AF. The result showed that three polymers were not viable choices for commercial applications and thus were eliminated. The eliminated materials were olefinic polymer, poly(siloctylene-siloxane) and Teflon AF. Table 3 summarizes the disadvantages of those three materials.

Table 3: The disadvantage of olefinic polymer, poly(siloctylene-siloxane) and Teflon AF

Material	Disadvantage
Olefinic polymer	Become too brittle when exposed to air during formation into spiral-wound module
Poly(siloctylene-siloxane)	Not commercially available anymore
Teflon AF	Selective for nitrogen over methane

The methane permeability and selectivity of other three polymers were determined from permeation test. Table 4 lists the properties of the membranes.

Table 4: Membrane Materials Chosen for Feasibility Study for Denitrogenation of Natural Gas. (Properties calculated from pure-gas measurements)

Polymer Type	Methane Permeability (10^{-10}cm^3(STP)·cm/ cm^2·s·cmHg)	CH_4/N_2 Selectivity at 23°C
Rubbery polymers (Tg < -50°C)		
Polyamide-polyether block copolymer (Pebax 2533)	20	4.2
Silicone rubber	760	3.3
Superglassy polymer (Tg >150°C)		
PTMSP	17,500	2.5

All the membranes are tested for the denitrogenation process with different feed temparatures. The result of the test will show whether the target selectivity can be achieved or not.

Table 5: Summary of permeability and selectivity of the three membranes tested.

Membrane Type	Feed Temperature (°C)	Methane Permeability Coefficient (10^{-10} cm³(STP)cm/cm²·s·cmHg)	Membrane Selectivity (-)		
			CH_4/N_2	C_3H_8/CH_4	C_3H_8/N_2
Silicone Rubber	20	638	2.6	3.1	8.4
	0	461	2.9	4.1	11.9
	-35	411	4.0	7.5	30.0
Pebax 2533	22	12.5	2.8	3.0	8.4
	-35	0.175	1.6	3.2	5.1
PTMSP	20	1,716	3.0	4.2	12.6
	0	1,760	3.7	6.7	24.9
	-55	2,552	5.5	11.5	74.1

From the results, it is concluded that Silicone rubber and PTMSP membrane are both good candidates for separation of nitrogen from natural gas. Both membrane achieved the target methane/nitrogen selectivity of 4-6 at temperature below -30°C, which is required for a viable process.

Figure 16 below shows the plot of methane/nitrogen selectivity for PTMSP membrane under various feed temperatures.

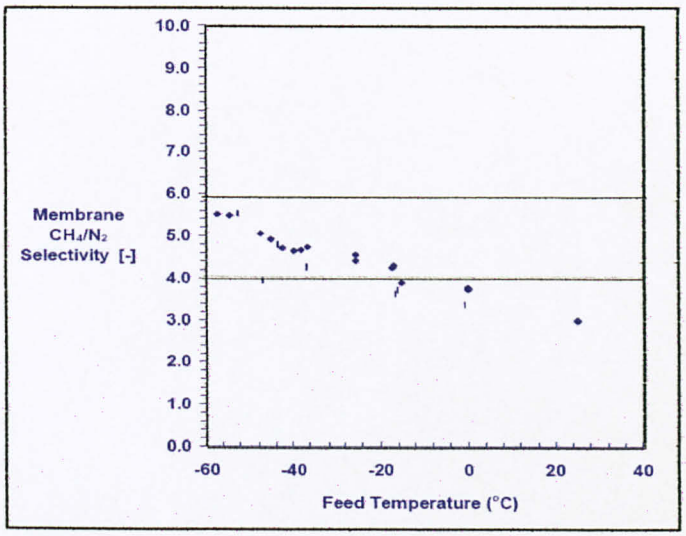


Figure 16: Methane/nitrogen selectivity as a function of feed temperature for the PTMSP membrane.

From the plot, it can be observed that the methane/nitrogen selectivity of 4-6 is achieved at temperature below -20°C. The selectivity in range of 5-6 is observed for the

temperature above -50°C (Kaaeid A. Lokhandwala, Matt Ringer, Hans Wijmans and Richard W. Baker).

From the research, it can be concluded silicone rubber and PTMSP are good membranes for denitrogenation of natural gas. Both membranes have methane/nitrogen selctivity of 4-6 at the temperature below -30°C (Kaaeid A. Lokhandwala, Matt Ringer, Hans Wijmans and Richard W. Baker).

CHAPTER 3
METHODOLOGY

For this project, the methodology is divided into three stage; Literature Review, Characterizations and Performance Study. Literature review and characterization are done to study the properties and performance of membrane. Literature review is done to obtain the membrane properties and the method to determine membrane characterizations. Characterizations lab is performed by using equipments obtained from literature review. In this project, three characterization studies are conducted; Scanning Electron Micrographic (SEM), Thermogravimetry Analysis (TGA) and Fourier Transform Infrared (FTIR) spectroscopy. After the membrane properties obtained from characterization study, dynamic study of membrane is conducted by using Gas Separation Unit to see the performance of membrane in removing water vapour from methane.

3.1 LITERATURE REVIEW

The purpose of this method is to study the theoretical facts and all the properties of membrane such as chemical bonding, surface area, type of material, permeability, pore size, porosity, thickness, symmetry, crystallization and etc. This is done by reviewing all the literature, journals and articles on membrane that can be obtained from internet and library. A few equipments are used in order to determine the membrane characteristics. From this study, the characters and properties of various types of membrane can be obtained. Thus comparisons can be made between flat typed membrane and other membranes. The properties of the flat membrane will help in determining the operating parameter such as pressure and temperature.

3.2 CHARACTERIZATIONS

From literature review, a lot of equipments can be used to determine properties of membrane such as SEM, FTIR, TGA, DMA, BET etc. Three equipments are available in UTP. The three experiments have been conducted to determine the characteristics of the

membrane; Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR) spectroscopy and Thermogravimetry Analysis (TGA).

3.2.1 Scanning Electron Microscope (SEM)

This experiment was conducted to observe the surface image of the membrane and its pore distribution. The image shows overall view of the membrane structure. This enables any symmetry to be observed.

Liquid nitrogen can be used to fracture the membrane before observing the sample using SEM. Unfortunately, in this work, the membrane can not be fractured under liquid nitrogen. Another method was used. A small part of membrane was chosen randomly and cut by using a sharpened razor blade. After being coated with gold paledium, the sample was observed using SEM with magnification of 100X to 50 K X.

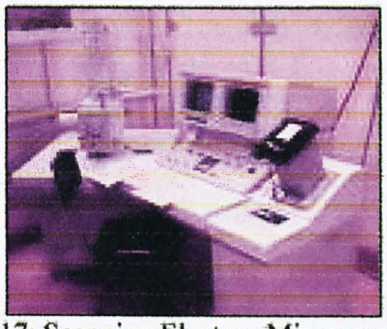


Figure 17: Scanning Electron Microscopy (SEM)

3.2.2 Fourier Transform Infrared (FTIR) spectroscopy

FTIR is used to identify compounds or investigate the membrane composition. FTIR is a chemical analytical technique, which measures the infrared intensity versus wavelength of light. The infrared spectrum of a sample is collected by passing a beam of infrared light through the sample. Examination of the transmitted light reveals how much energy was absorbed at each wavelength. This can be done with a monochromatic beam, which changes in wavelength over time, or by using a Fourier Transform instrument to measure all wavelengths at once. From this, a transmittance or absorbance spectrum can be produced,

showing at which IR wavelengths the sample absorbs. Analysis of these absorption characteristics reveals details about the molecular structure of the sample (Wikipedia, 2009).

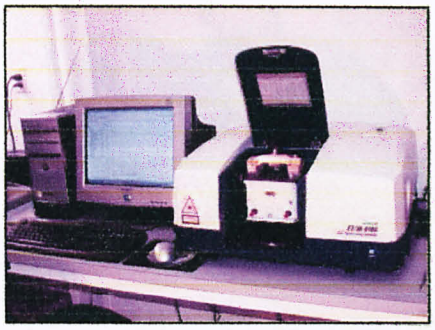


Figure 18: Fourier Transform Infrared (FTIR) spectroscopy

In this experiment, a small part of membrane was cut and analyzed by using FTIR. A plot of Transmitter (%) versus wavelength was produced. From this wavelength, the components of the membrane can be analyzed.

3.1.2 Thermo Gravimetric Analysis (TGA)

Thermo Gravimetric Analysis equipment is used to identify the degradation temperature of membrane. The degradation temperature will be used to determine the maximum temperature to operate the membrane. If the membrane is operated at higher temperature than its degradation temperature, it might get burnt or damaged.

For this experiment, a small part of membrane with the weight of 4.45 mg was cut and the sample is burnt slowly in the furnace of TGA system. The plot of weight percent versus temperature is produced.

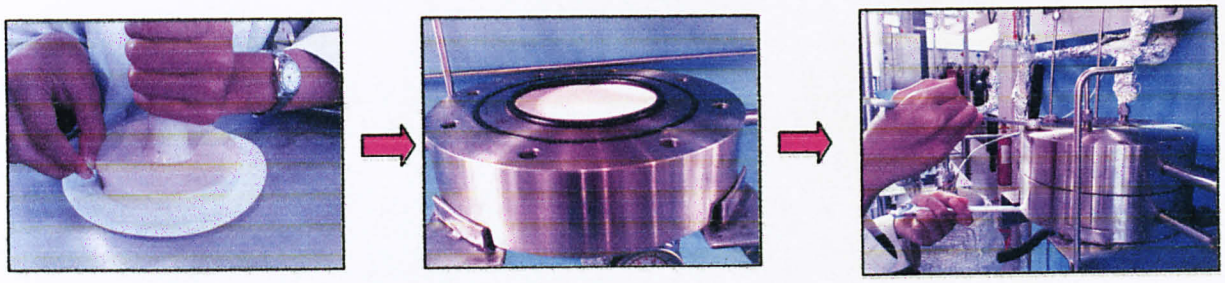
Figure 19: Thermogravimetric Analysis equipment

3.2 PARAMETRIC ANALYSIS

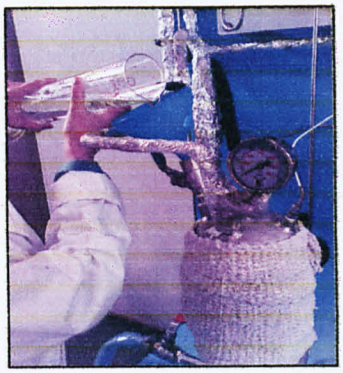
Experimental lab is conducted to test the performance of the membrane in removing water from natural gas. The operating pressure is varied to test the performance of the membrane under various pressures. The performance test is the indicator to determine the efficiency of the membrane in removing water from natural gas.

Equipment used for the experiment is Gas Separation Unit. Membrane in flat module is inserted into a membrane test cell and the methane with water vapour will pass through it. The thickness of the membrane is 134.8 μm and the diameter is 11 cm. The procedures of the experiment are as following:

1. Membrane is cut to diameter of 11 cm and put in the membrane test cell.



2. The saturation vessel is filled with 250 ml of water.



3. The saturation vessel is heated to 50°C.
4. The valve of the methane cylinder is opened to allow the flow of methane gas in pipeline. The flow rate of the methane is set at 5 LPM and the pressure is set at 10 bar.
5. The methane inserts the saturation vessel where it is wetted with water vapour.

6. The mixture of methane and water vapour exits from saturation vapour. The amount of water vapour in the outlet will be measured by a moisture analyzer located at the outlet of saturation vessel.
7. The mixture of methane and water vapour flows to membrane column, where separation process will take place.
8. The amount of water in the retentate (methane) is determined by a moisture analyzer at the outlet of the membrane column.
9. The permeate (water vapour) is ventilated out.
10. Amount of water removed by the membrane is calculated.

    Percentage of water removed:

$$\frac{\text{Water concentration in the saturation vessel outlet} - \text{water concentration in the retentate outlet}}{\text{Water concentration in the saturation vessel outlet}} \times 100\%$$

11. Procedures 4 to 10 are repeated for pressure of 20 bar to 80 bar (the maximum pressure, the membrane will damage if the pressure exceed 80 bar), while the flow rate is remained at 5 NLPM.

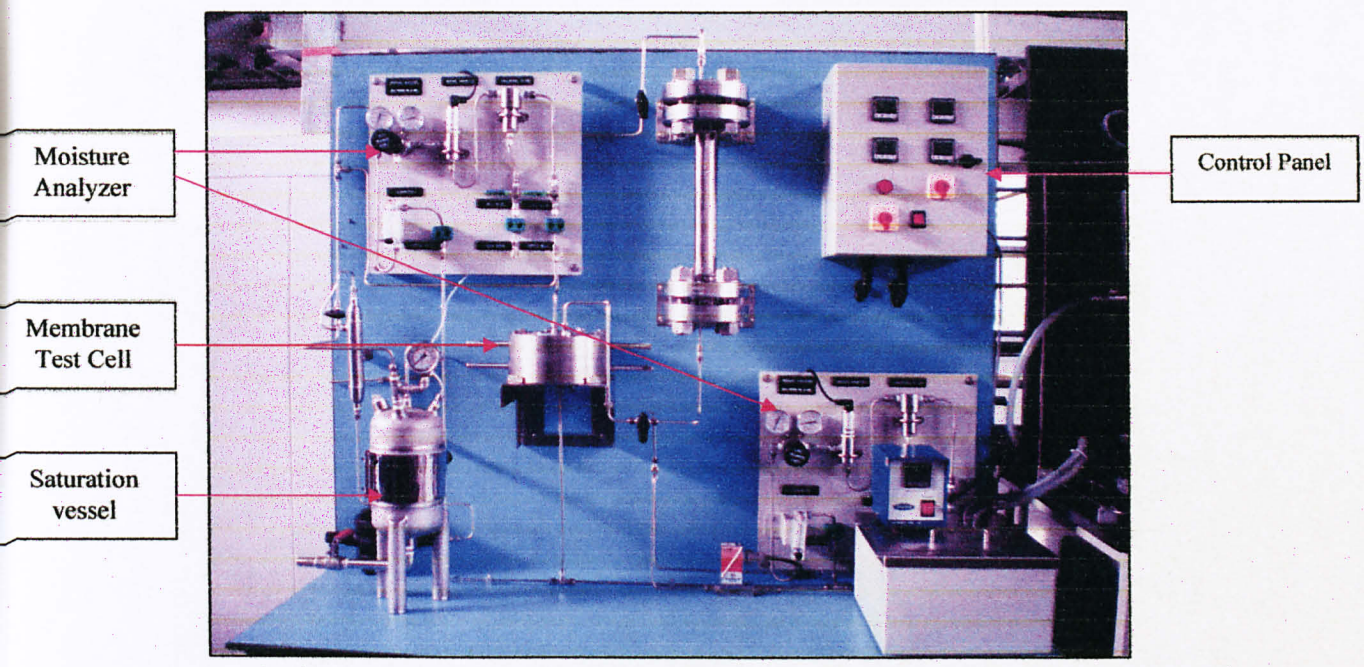


Figure 20: Gas Separation Unit

CHAPTER 4
RESULTS AND DISCUSSION

4.1 CHARACTERIZATIONS STUDY

4.1.1 Structure of Membrane

Figures below show the top surface and cross section structures of membrane observed by using SEM.

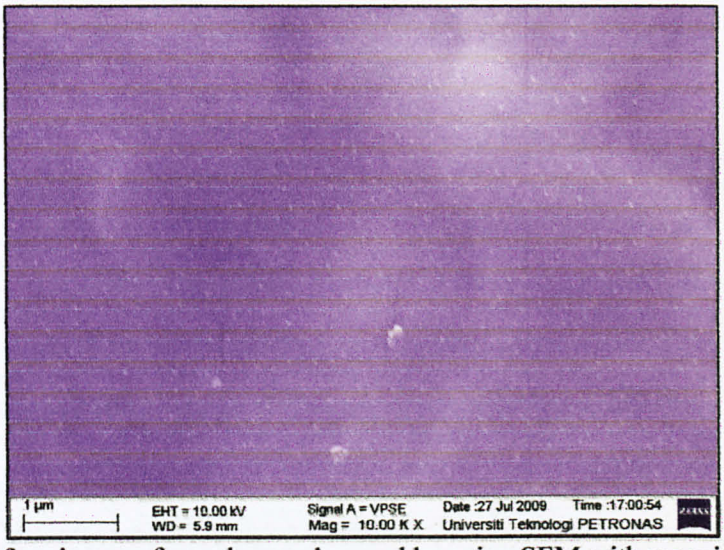


Figure 21: Top surface image of membrane observed by using SEM with magnification of 10 K X.

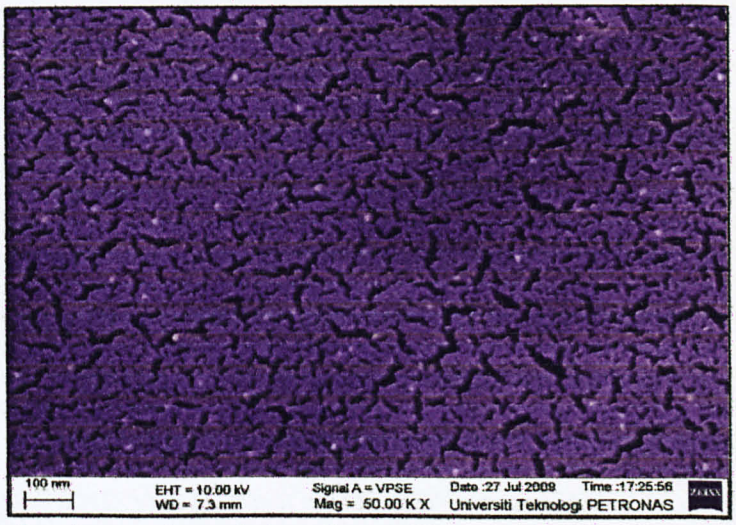


Figure 22: Top surface image of membrane observed by using SEM with magnification of 50 K X.

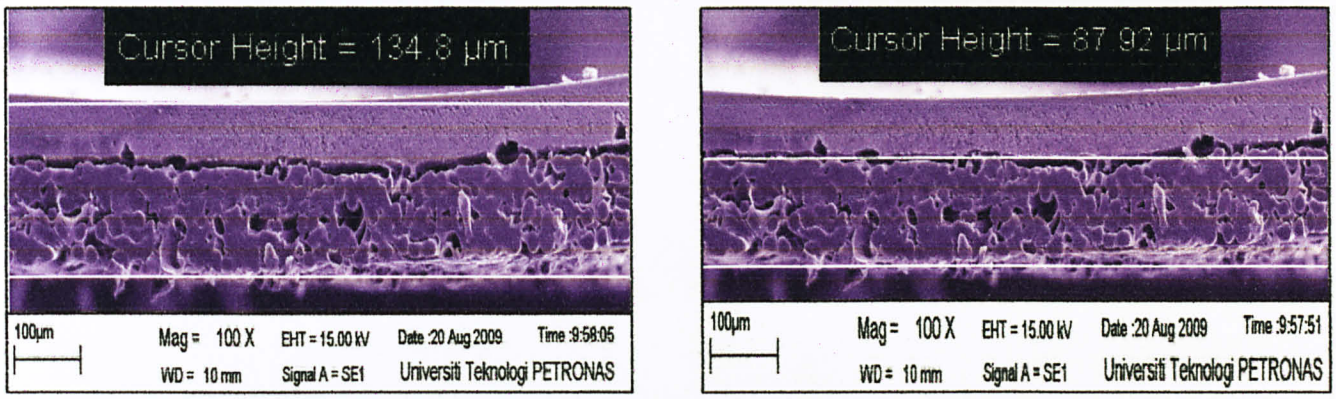


Figure 23: Cross section structure of membrane observed by using SEM with magnification of 100 X.

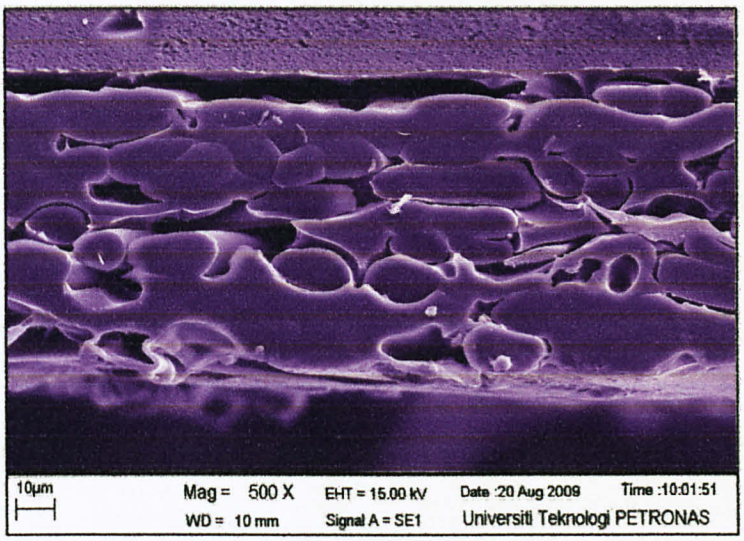


Figure 24: Cross section structure of membrane observed by using SEM with magnification of 500 X.

From the images observed by SEM, we can conclude that the membrane is asymmetric, since it consists of two structural planes of non-identical morphologies. The membrane has dense top layer and porous substructure.

The thickness of the membrane is 134.8 µm, while the thickness of the porous substructure is 87.92 µm. From literature review, the porous substructure of an integrally skinned and dense top layer membrane has the thickness between 50 µm to 150 µm (Chen, 2002). Thus we can classify the membrane as an integrally skinned and dense top layer membrane.

4.1.2 Components of Membrane

FTIR is used to identify the functional groups in the membrane. The data can be used to identify if the membrane is made of hydrocarbon-based polymers. Natural gas has small amounts of aliphatic and aromatic hydrocarbons. They are highly soluble in hydrocarbon-based membrane and can plasticize polymer membranes, reducing the diffusion-selectivity of the membranes (Chemical and Engineering News, 3rd October 2005, *Membranes for Gas Separation*).

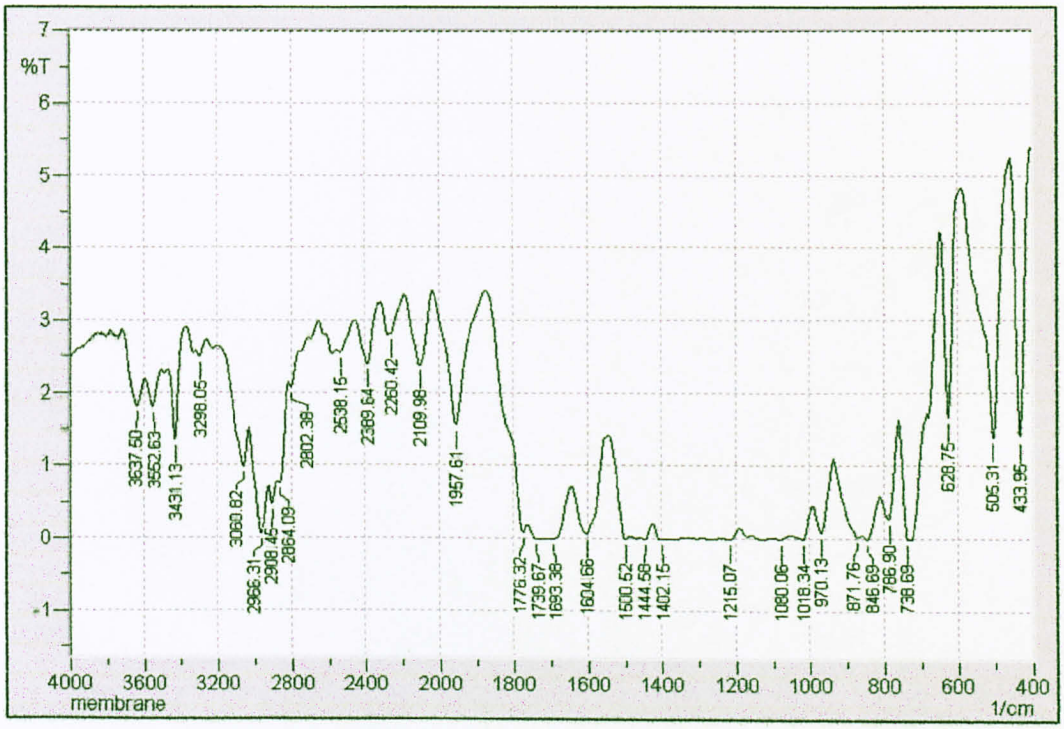


Figure 25: Plot of transmitter (%) versus wavelength obtained from FTIR

From the data, components of the membrane can be determined by using the wavelengths. The wavelengths are different for each functional group. The components and functional groups of each wavelength in the plot are shown in the table below:

Table 6: Components and functional group analyzed from FTIR data.

Wavelength (cm^{-1})	Components	Functional Group
433.95	Aryl disulfides	S-S
505.31	Iodoalkanes	C-I
628.75	Bromoalkanes	C-Br
738.69	Chloroalkanes	C-Cl
786.90	Chloroalkanes	C-Cl
846.69	Aryl	C-H
871.76	Aryl	C-H
970.13	Aryl	C-H
1018.34	Fluoroalkanes	C-F
1080.06	Amine	N-H
1215.07	Aryl	C-H
1402.15	Phenol	O-H
1444.58	Methyl	C-H
1500.52	Aryl	C-H
1604.66	Amine	N-H
1693.38	Carbonyl	C=O
1739.67	Carbonyl	C=O
1776.32	Carbonyl	C=O
1957.61	Aryl	C-H
2109.98	Alkyne	C-H
2260.42	Alkyne	C-H
2538.15	Ammonium ion	N-H
2802.38	Methyl amino	N-H
2864.09	Methyl	C-H
2908.45	Methylene	C-H
2966.31	Methyl	C-H
3060.82	Ammonium ion	N-H
3298.05	Phenol	O-H
3431.13	Amine	N-H

3552.63	Carboxylic acid	O-H
3637.50	Phenol	O-H

From the results, it can be concluded that the membrane has more than three functional groups. The membrane consists of mainly O-H, N-H, C=O and C-H groups. It is concluded that the membrane made of hydrocarbon-based polymer. Thus the effect of aliphatic and aromatic hydrocarbon to the membrane have to be considered in this research.

4.1.3 Degradation Temperature

Degradation temperature of membrane will be used to determine the maximum operating temperature of the membrane. TGA is used to observe the changes in membrane weight in relation to change in temperature. A plot of weight percent versus temperature is produced from the experiment.

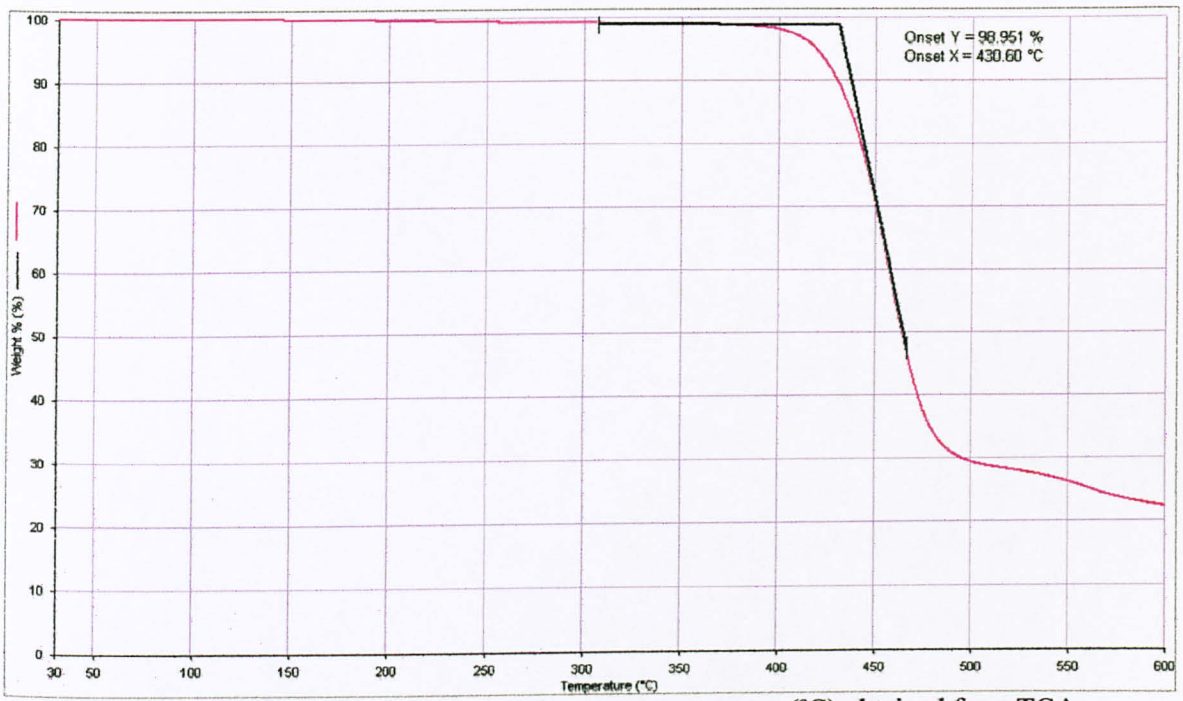


Figure 26: Plot of weight percent (%) versus temperature (°C) obtained from TGA

From the result, it is observed that as the temperature increases, the weight percent of the membrane decreases. It indicated that the longer the membrane is burnt, the weight of the membrane becomes decrease. From temperature of 30°C, the weight of the membrane

decreases slowly, until it reaches 400°C. In the range of 400°C to 500°C, the weight of the membrane decreases significantly and the slope is steeper.

From the tangent produced in the plot, it is observed that the degradation temperature of the membrane is 430.60°C. Thus it can be concluded that the membrane can not be operated with the temperature higher than 430.60°C.

4.2 PARAMETRIC ANALYSIS

4.2.1 Calibration Curve

Calibration is done to determine the best temperature to run the experiment. The inlet pressure used is in the range of 20-60 barg. For each pressure, temperature is manipulated from 40, 45 and 50 °C. The inlet flow rate is constant at 5 LPM.

Table 7: Inlet moisture content at various temperature and pressure

Inlet temperature (°C)	Pressure (barg)	Inlet Dew Point (°C)	Moisture concentration (ppm_v)
40	20	17.2	923.389
	40	15.0	410.756
	60	14.7	270.755
45	20	17.2	923.389
	40	15.7	429.655
	60	15.5	285.064
50	20	20.0	1100.570
	40	17.1	469.756
	60	17.2	317.696

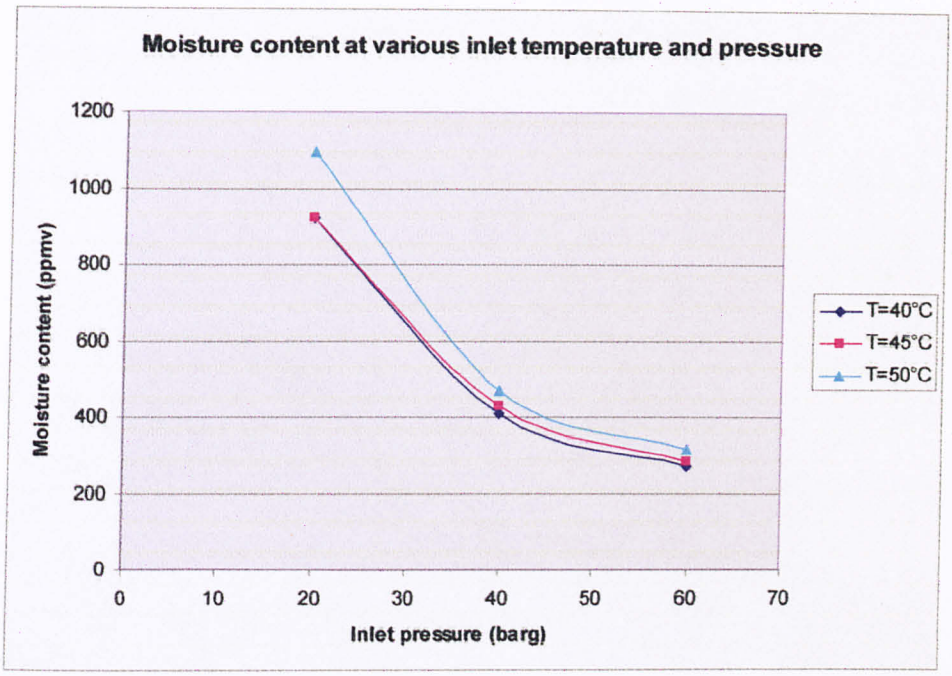


Figure 27: Plot of moisture content versus pressure at different inlet temperature.

The plot shows that as the temperature increases, the moisture content will be increased. As for the effect of inlet pressure, the plot shows that the moisture content is inversely proportional with inlet pressure. The moisture content decreases as the inlet temperature is increased. This means that at low pressure and high temperature, the concentration of water vapour in methane increases.

From the plot, temperature of 50°C has the highest concentration of water compared to 40°C and 45°C. Thus, it is decided to run the experiment at temperature of 50°C.

4.2.2 Water Vapour Removal by Membrane

From experiment lab, the percent of water vapour removal from methane by membrane can be calculated. The percent of water vapour removal at different inlet pressure indicate the efficiency of membrane in removing water vapour from methane. Pressure is the only manipulated parameter in this study. Other parameters, temperature and flow rate are constant at 50°C and 5 NLPM.

Table 8: Percentage of water vapour removal at various inlet pressures

Pressure (barg)	Inlet Flow Rate (LPM)	Dew Point Inlet (°C)	Dew Point Outlet (°C)	Inlet Concentration (PPM)	Outlet Concentration (PPM)	% Water Vapour Removal
10	5	20.4	9.1	2155.991	1038.248	51.84
20	5	20.4	8.0	1128.171	504.497	55.28
30	5	20.4	6.5	763.966	308.324	59.64
40	5	20.4	4.5	577.526	202.859	64.87

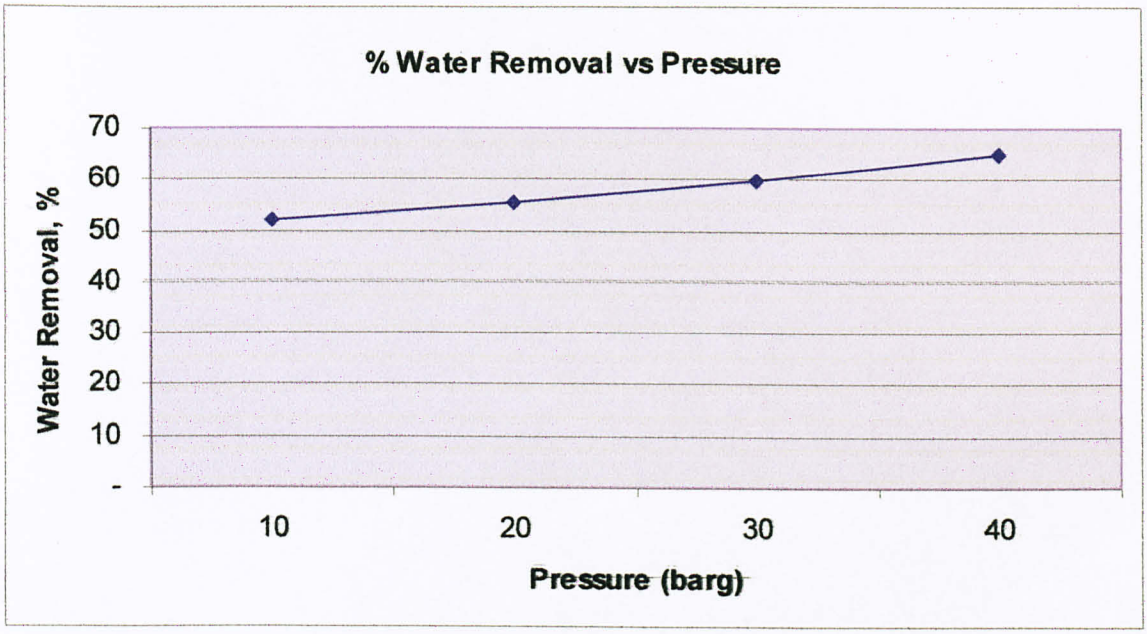


Figure 28: Plot of water removal percentage at different inlet pressure.

It is obtained from the plot that the percentage of water vapour removal increases as the pressure increases. Thus it can be concluded that at high pressure, the membrane separates more water vapour from methane gas. At high pressure, the flux of water vapour through the membrane is high, thus the water vapour removal increases.

4.2.3 Percent of Hydrocarbon Loss

During the experiment, flow rate of retentate stream is measured. Mass balance is done to calculate the flow rate of permeate stream. Permeate flow rate is used to calculate the hydrocarbon loss.

Table 9: Percentage of hydrocarbon loss at various inlet pressures

Pressure (barg)	Inlet Flow Rate (LPM)	Retentate Flow Rate (LPM)	Permeate Flow rate (LPM)	% Hydrocarbon Loss
10	5	3.33	0.67	16.75
20	5	2.67	1.33	33.25
30	5	2.00	2.00	50.0
40	5	1.87	2.13	53.25

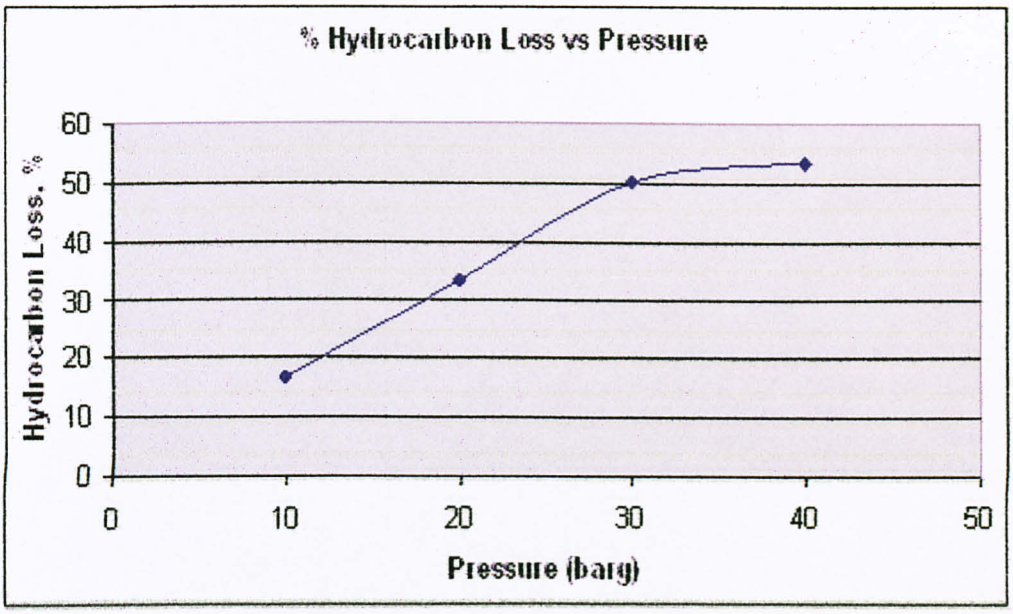


Figure 29: Plot of hydrocarbon loss at different inlet pressure.

From the plot, it is observed that as the pressure increases, the hydrocarbon loss also increases. As the pressure increases, the flow rate of permeate stream is increasing. A lot of hydrocarbon escape to the permeate stream, thus increasing the hydrocarbon loss of the system.

4.2.4 Comparison between Water Vapour Removal and Hydrocarbon Loss

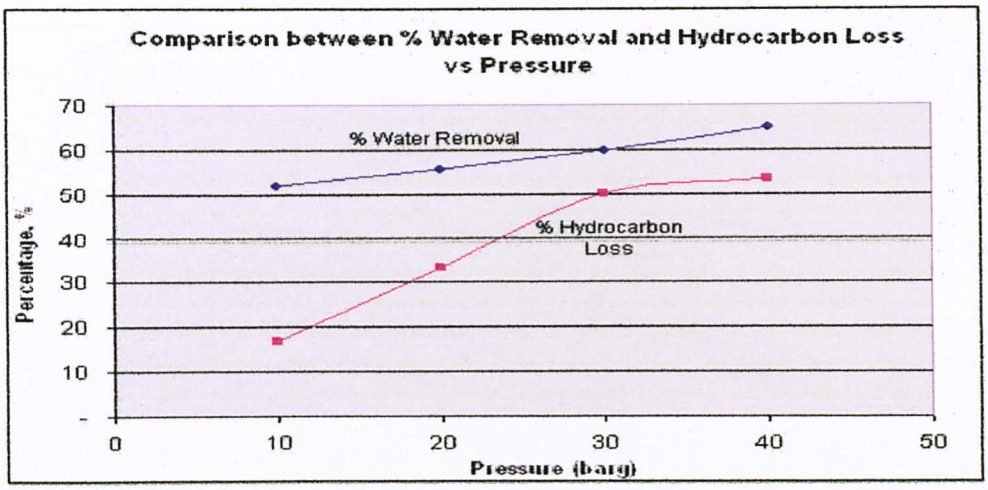


Figure 30: Comparison between water removal and hydrocarbon loss.

From the plot, it can be observed as the pressure increases, both water vapour removal and hydrocarbon loss also increase. A good membrane will obtain high water vapour removal and low hydrocarbon loss. From the results obtained, optimization should be conducted to determine the optimum operating pressure to operate the membrane. Since this study only focus on performance of membrane, the optimum operating pressure is not determined. Thus it is recommended to conduct the optimization based on cost analysis in the next study.

CHAPTER 5
CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

Operational problems occur to TEG system make it necessary to find other alternatives to remove water vapour from natural gas. TEG system need big footprints, where as offshore platforms have limited space. Membrane separation is one of the alternatives to remove water vapour from natural gas at offshore platforms. Even though it might be costly, but it can save the space in offshore since offshore platform has limited space.

Glassy polymer membrane is believed to be the best membrane for gas separation. Among glassy polymer membranes commonly used in industry are polysulfone, polyimide and polycarbonate.

From the images observed by SEM, it is concluded that the membrane is asymmetric, since it has dense top layer and porous substructure. The membrane is classified as an integrally skinned and dense top layer membrane.

From FTIR, we know that the membrane has more than three functional groups, including O-H, C-H, N-H, C=O and etc. The membrane consists of mainly O-H, N-H, C=O and C-H groups.

For TGA analysis, it is concluded that the maximum temperature to operate the membrane is 430.60°C. High temperature exceed the maximum temperature might cause damage to the membrane.

From the experiment, it is obtained that water vapour removal from methane increases as the pressure increases. Thus it can be concluded that the membrane separate more water vapour from methane at high pressure. For hydrocarbon loss, it is concluded that the hydrocarbon loss also increases as pressure increases. The membrane is good in removing

water vapour from methane, but optimization need to be conducted to minimize hydrocarbon loss by the membrane.

As the conclusion, the objective to analyze the performance of membrane under various operating pressure is achieved.

5.2 RECOMMENDATIONS

Based on the results obtained from the experiment, it is recommended that optimization is conducted in the next study. The optimum pressure can be determined by optimization based on cost analysis to maximize water vapour removal and minimize hydrocarbon loss.

During the experiment, some moisture might be condensed along the pipeline. Thus, it is suggested to shorten the pipeline to minimize condensation. Heaters are recommended to be installed right before the membrane inlet and moisture analyzer.

REFERENCES

Alia Najihah. 2004, *Separation of Moisture from Natural Gas Using Membrane Separation (Modelling)*, Final Year Project Thesis, UTP

Chemical and Engineering News, 3rd October 2005, *Membranes for Gas Separation*

Cristie John Geankoplis. 2003, *Transport Processes of Separation Process Principle*, Fourth Edition, Prentice Hall

F.Binci, F.E. Ciarapica and G.Giacchetta, *Natural Gas Dehydration In Offshore Rigs : Comparison Between Traditional Glycol Plants And Innovative Membrane Systems*, Department of Energetics, Faculty of Engineering, University of Anconavia Brecce Bianche, 60131, Ancona, Italy

Kaaeid A. Lokhandwala, Matt Ringer, Hans Wijmans and Richard W. Baker, *Nitrogen Removal From Natural Gas Using Membrane,* **Membrane Technology and Research, Inc.**

Keith Scott, *Handbook of Industrial Membranes*

Muhammad Iqbal, 2007, *Development of Asymmetric Polycarbonate (PC) Membrane for Carbon Dioxide Removal from Methane*, Master Project Thesis, UTP

Nur Zuraini bt Zailani, 2003, *Separation of Hydrogen Sulfide from Methane by Using Membrane Technology*, Final Year Project Thesis, UTP

S.P. Nunes and K.-V. Peinemann. 2001, *Membrane Technology in the Chemical Industry*, Wiley-VCH

Takeshi Matsuura, 1993, Synthetic *Membranes and Membrane Separation Processes*, CRC Press Inc

US Patent Application 20070151447 - *Gas Separation Membranes And Processes For Controlled Environmental Management*

US Patent Application 20060174762 - *Gas Separation Membrane Module Assembly*

US Patent 5256296 - *Membrane Process And Apparatus For Removing A Component From A Fluid Stream*

Warren L. McCabe, Julian C. Smith and Peter Harriott. 2005, *Unit Operations of Chemical Engineering*, Seventh Edition, McGraw Hill International Edition

Yoshihito Osada and Tsutomu Nakagawa, 1992, *Membrane Science and Technology*, Mercel Dekker Inc.

http://www.naturalgas.org/overview/uses_industry.asp

http://www.pge.com/microsite/safety_esw_ngsw/ngsw/efficiently/uses.html

http://www.naturalgas.org/overview/uses.asp

http://en.wikipedia.org/wiki/Natural_gas

http://en.wikipedia.org/wiki/Scanning_electron_microscope

http://en.wikipedia.org/wiki/Fourier_transform_infrared_spectroscopy

APPENDICES

Appendix 1: FTIR Data Analysis

Table 10: Functional groups with their wavelengths used for FTIR data analysis

Bond	Type of bond	Specific type of bond	Absorption peak	Appearance
C—H	alkyl	methyl	1260 cm^{-1}	strong
			1380 cm^{-1}	weak
			2870 cm^{-1}	medium to strong
			2960 cm^{-1}	medium to strong
		methylene	1470 cm^{-1}	strong
			2850 cm^{-1}	medium to strong
			2925 cm^{-1}	medium to strong
		methine	2890 cm^{-1}	weak
	vinyl	$C{=}CH_2$	900 cm^{-1}	strong
			2975 cm^{-1}	medium
			3080 cm^{-1}	medium
		C≡CH	3020 cm^{-1}	medium

		monosubstituted alkenes	900 cm^{-1}	strong
			990 cm^{-1}	strong
		cis-disubstituted alkenes	670–700 cm^{-1}	strong
		trans-disubstituted alkenes	965 cm^{-1}	strong
		trisubstituted alkenes	800–840 cm^{-1}	strong to medium
	aromatic	benzene/sub. benzene	3070 cm^{-1}	weak
		monosubstituted benzene	700–750 cm^{-1}	strong
			690–710 cm^{-1}	strong
		ortho-disub. benzene	750 cm^{-1}	strong
		meta-disub. benzene	750–800 cm^{-1}	strong
			860–900 cm^{-1}	strong
		para-disub. benzene	800–860 cm^{-1}	strong

	alkynes	any	3300 cm^{-1}	medium
	aldehydes	any	2720 cm^{-1}	medium
			2820 cm^{-1}	
C—C	acyclic C—C	monosub. alkenes	1645 cm^{-1}	medium
		1,1-disub. alkenes	1655 cm^{-1}	medium
		cis-1,2-disub. alkenes	1660 cm^{-1}	medium
		trans-1,2-disub. alkenes	1675 cm^{-1}	medium
		trisub., tetrasub. alkenes	1670 cm^{-1}	weak
	conjugated C—C	dienes	1600 cm^{-1}	strong
			1650 cm^{-1}	strong
	with benzene ring		1625 cm^{-1}	strong
	with C=O		1600 cm^{-1}	strong
	C=C (both sp^2)	any	1640–1680 cm^{-1}	medium
	aromatic C=C	any	1450 cm^{-1}	weak to strong (usually 3

			1500 cm^{-1}	or 4)
			1580 cm^{-1}	
			1600 cm^{-1}	
	C≡C	terminal alkynes	2100–2140 cm^{-1}	weak
		disubst. alkynes	2190–2260 cm^{-1}	very weak (often indisinguishable)
C=O	aldehyde/ketone	saturated aliph./cyclic 6-membered	1720 cm^{-1}	
		α,β-unsaturated	1685 cm^{-1}	
		aromatic ketones	1685 cm^{-1}	
		cyclic 5-membered	1750 cm^{-1}	
		cyclic 4-membered	1775 cm^{-1}	
		aldehydes	1725 cm^{-1}	influence of conjugation (as with ketones)
	carboxylic acids/derivates	saturated carboxylic acids	1710 cm^{-1}	
		unsat./aromatic carb. acids	1680–1690 cm^{-1}	

		esters and lactones	1735 cm^{-1}	influenced by conjugation and ring size (as with ketones)
		anhydrides	1760 cm^{-1}	
			1820 cm^{-1}	
		acyl halides	1800 cm^{-1}	
		amides	1650 cm^{-1}	associated amides
		carboxylates (salts)	1550–1610 cm^{-1}	
		amino acid zwitterions	1550–1610 cm^{-1}	
O–H	alcohols, phenols	low concentration	3610–3670 cm^{-1}	
		high concentration	3200–3400 cm^{-1}	broad
	carboxylic acids	low concentration	3500–3560 cm^{-1}	
		high concentration	3000 cm^{-1}	broad
N–H	primary amines	any	3400–3500 cm^{-1}	strong
			1560–1640	strong

			cm^{-1}	
	secondary amines	any	>3000 cm^{-1}	weak to medium
	ammonium ions	any	2400–3200 cm^{-1}	multiple broad peaks
C–O	alcohols	primary	1040–1060 cm^{-1}	strong, broad
		secondary	~1100 cm^{-1}	strong
		tertiary	1150–1200 cm^{-1}	medium
	phenols	any	1200 cm^{-1}	
	ethers	aliphatic	1120 cm^{-1}	
		aromatic	1220–1260 cm^{-1}	
	carboxylic acids	any	1250–1300 cm^{-1}	
	esters	any	1100–1300 cm^{-1}	two bands (distinct from ketones, which do not possess a C–O bond)
C–N	aliphatic amines	any	1020–1220 cm^{-1}	often overlapped
	C=N	any	1615–1700 cm^{-1}	similar conjugation effects to C=O

	C≡N (nitriles)	unconjugated	2250 cm^{-1}	medium
		conjugated	2230 cm^{-1}	medium
	R—N—C (isocyanides)	any	2165–2110 cm^{-1}	
	R—N=C=S	any	2140–1990 cm^{-1}	
C—X	fluoroalkanes	ordinary	1000–1100 cm^{-1}	
		trifluromethyl	1100–1200 cm^{-1}	two strong, broad bands
	chloroalkanes	any	540–760 cm^{-1}	weak to medium
	bromoalkanes	any	500–600 cm^{-1}	medium to strong
	iodoalkanes	any	500 cm^{-1}	medium to strong
N—O	nitro compounds	aliphatic	1540 cm^{-1}	stronger
			1380 cm^{-1}	weaker
		aromatic	1520, 1350 cm^{-1}	lower if conjugated

Appendix 2: TGA Results

Table 11: Data table of temperature and weight percent of membrane obtained from TGA

Temperature (°C)	Weight % (%)	Temperature (°C)	Weight % (%)	Temperature (°C)	Weight % (%)
28.84	99,997	238,84	99,441	448,84	72,752
33.84	100,027	243,84	99,412	453,84	65,538
38.84	100,03	248,84	99,387	458,84	58,121
43.84	100,022	253,84	99,363	463,84	50,836
48.84	100,014	258,84	99,342	468,84	44,25
53.84	100,011	263,84	99,32	473,84	38,806
58.84	100,003	268,84	99,299	478,84	35,037
63.84	99,999	273,84	99,28	483,84	32,658
68.84	99,996	278,84	99,262	488,84	31,134
73.84	99,993	283,84	99,248	493,84	30,157
78.84	99,991	288,84	99,23	498,84	29,494
83.84	99,99	293,84	99,212	503,84	29,065
88.84	99,984	298,84	99,202	508,84	28,74
93.84	99,983	303,84	99,183	513,84	28,484
98.84	99,985	308,84	99,167	518,84	28,246
103.84	99,981	313,84	99,154	523,84	28,001
108.84	99,975	318,84	99,141	528,84	27,731
113.84	99,981	323,84	99,123	533,84	27,438
118.84	99,968	328,84	99,103	538,84	27,101
123.84	99,96	333,84	99,088	543,84	26,714
128.84	99,949	338,84	99,07	548,84	26,273
133.84	99,939	343,84	99,047	553,84	25,788
138.84	99,926	348,84	99,028	558,84	25,271
143.84	99,912	353,84	99,003	563,84	24,742
148.84	99,899	358,84	98,975	568,84	24,249
153.84	99,883	363,84	98,944	573,84	23,823
158.84	99,867	368,84	98,907	578,84	23,458
163.84	99,851	373,84	98,86	583,84	23,14
168.84	99,834	378,84	98,799	588,84	22,849
173.84	99,815	383,84	98,713	593,84	22,576
178.84	99,783	388,84	98,594	598,84	22,308
183.84	99,771	393,84	98,433	603,84	22,045
188.84	99,744	398,84	98,2		
193.84	99,719	403,84	97,811		
198.84	99,694	408,84	97,232		
203.84	99,664	413,84	96,389		
208.84	99,633	418,84	95,184		
213.84	99,605	423,84	93,426		
218.84	99,574	428,84	90,899		
223.84	99,535	433,84	87,85		
228.84	99,508	438,84	83,815		
233.84	99,471	443,84	78,781		

Table 12: Data table of temperature and weight of membrane (mg) obtained from TGA

Temperature (°C)	Weight (mg)	Temperature (°C)	Weight (mg)	Temperature (°C)	Weight (mg)
28,84	4,447	238,84	4,422	448,84	3,235
33,84	4,448	243,84	4,421	453,84	2,914
38,84	4,448	248,84	4,42	458,84	2,585
43,84	4,448	253,84	4,419	463,84	2,261
48,84	4,448	258,84	4,418	468,84	1,968
53,84	4,448	263,84	4,417	473,84	1,726
58,84	4,447	268,84	4,416	478,84	1,558
63,84	4,447	273,84	4,415	483,84	1,452
68,84	4,447	278,84	4,414	488,84	1,385
73,84	4,447	283,84	4,414	493,84	1,341
78,84	4,447	288,84	4,413	498,84	1,312
83,84	4,447	293,84	4,412	503,84	1,293
88,84	4,446	298,84	4,411	508,84	1,278
93,84	4,446	303,84	4,411	513,84	1,267
98,84	4,446	308,84	4,41	518,84	1,256
103,84	4,446	313,84	4,409	523,84	1,245
108,84	4,446	318,84	4,409	528,84	1,233
113,84	4,446	323,84	4,408	533,84	1,22
118,84	4,446	328,84	4,407	538,84	1,205
123,84	4,445	333,84	4,406	543,84	1,188
128,84	4,445	338,84	4,406	548,84	1,168
133,84	4,444	343,84	4,405	553,84	1,147
138,84	4,444	348,84	4,404	558,84	1,124
143,84	4,443	353,84	4,403	563,84	1,1
148,84	4,443	358,84	4,401	568,84	1,078
153,84	4,442	363,84	4,4	573,84	1,059
158,84	4,441	368,84	4,398	578,84	1,043
163,84	4,44	373,84	4,396	583,84	1,029
168,84	4,44	378,84	4,394	588,84	1,016
173,84	4,439	383,84	4,39	593,84	1,004
178,84	4,437	388,84	4,384	598,84	0,992
183,84	4,437	393,84	4,377	603,84	0,98
188,84	4,436	398,84	4,367		
193,84	4,434	403,84	4,35		
198,84	4,433	408,84	4,324		
203,84	4,432	413,84	4,286		
208,84	4,431	418,84	4,233		
213,84	4,429	423,84	4,155		
218,84	4,428	428,84	4,042		
223,84	4,426	433,84	3,907		
228,84	4,425	438,84	3,727		
233,84	4,423	443,84	3,503		

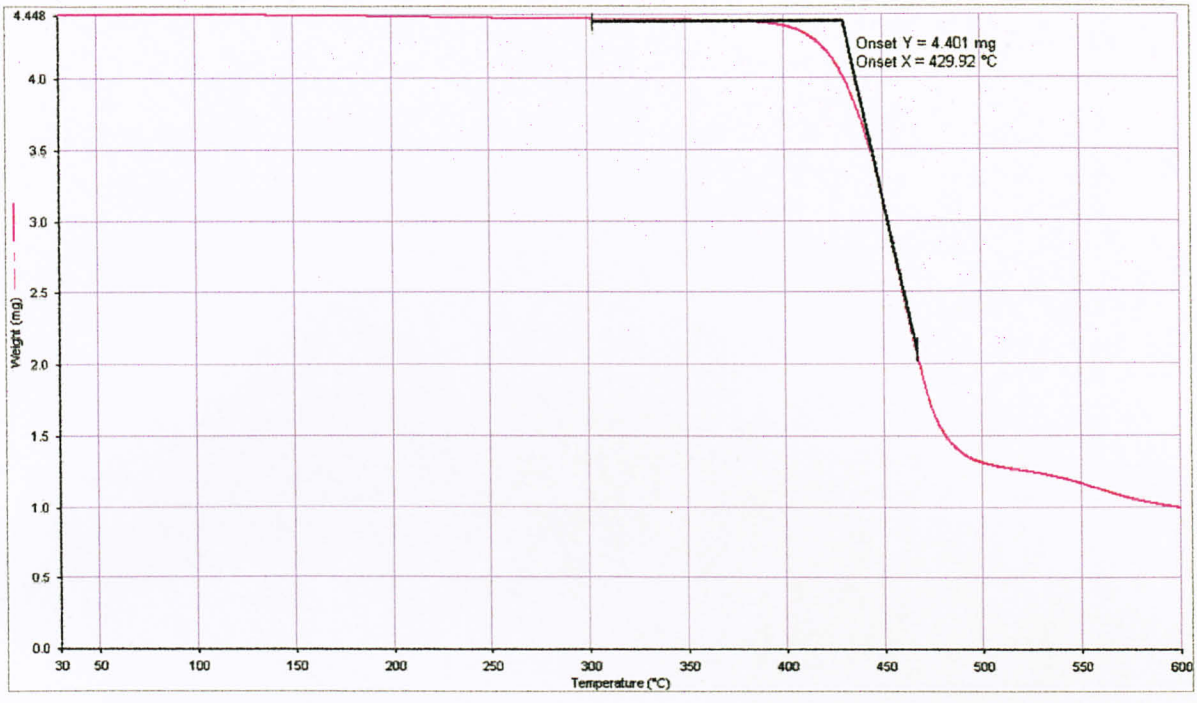


Figure 31: Plot of weight (mg) versus temperature (°C) obtained from TGA

Appendix 3: Sample Calculations

1) Water Removal Calculation

Percentage of water vapour removed:

$$\frac{\text{Water concentration in the saturation vessel outlet} - \text{water concentration in the retentate outlet}}{\text{Water concentration in the saturation vessel outlet}} \times 100\%$$

At pressure 10 barg and temperature 50°C, the inlet moisture is 2155.991 ppm_v and the outlet moisture is 1038.248 ppm_v.

$$\text{Percentage of water vapour removed} = \frac{2155.991\ ppm_v - 1038.248\ ppm_v}{2155.991\ ppm_v} \times 100\%$$

$$= \mathbf{51.84\ \%}$$

2) Permeate Flow Rate Calculation

Permeate flow rate = Inlet flow rate – Inlet moisture analyzer flow rate – Retentate flow rate

At pressure 10 barg: Inlet flow rate = 5 LPM, Inlet moisture analyzer flow rate = 1 LPM,
Retentate flow rate = 3.33 LPM

Permeate flow rate = 5 LPM – 1 LPM – 3.33 LPM

$$= \mathbf{0.67\ LPM}$$

3) Hydrocarbon Loss Calculation

$$\text{Percentage of hydrocarbon loss} = \frac{\text{Flow rate of membrane inlet} - \text{Flowrate of permeate}}{\text{Flow rate of membrane inlet}} \times 100\%$$

At pressure 10 barg, the flow rate of membrane inlet is 5 LPM and the flow rate of permeate stream is 0.67 LPM

Percentage of hydrocarbon loss = $\frac{5 \text{ LPM} - 0.67 \text{ LPM}}{5 \text{ LPM}} \times 100\%$

= **16.75 %**